ABSTRACT

CORA NICHOLS: Factors Affecting the Formation and Decay of Trihalomethanes and Haloacetic Acids in a Full-Scale Drinking Water Distribution System.
(Under the direction of Dr. Philip C. Singer)

The formation and decay of trihalomethanes (THMs) and haloacetic acids (HAAs) were evaluated in a full-scale distribution system where free chlorine and combined chlorine were used as secondary disinfectants. The distribution system was monitored over a 4-month period, while the utility switched from combined chlorine to free chlorine for a one-month period and then back to combined chlorine. A distribution system model was used to identify 14 sample sites representing a wide variety of point of use attributes including residence time, pipe diameter, and pipe material.

The results show that free chlorine dissipated in the distribution system proportionally to residence time, while the combined chlorine residual remained stable. The disinfection by-product (DBP) concentrations in the distribution system varied with disinfectant type, dose, and contact time. Free chlorine disinfection produced significantly higher DBP concentrations than combined chlorine. DBP concentrations were relatively stable throughout the distribution system during chloramination, but continued to increase with increasing residence time during chlorination. The THM concentration increased more significantly than the HAA concentration as residence time increased. Accordingly, the THM to HAA ratio increased with increasing residence time during chlorination. There was no discernable impact of pipe diameter or pipe material on DBP formation or decay. No biological degradation of HAAs was observed during this study. HPC concentrations were unaffected by the switch from combined chlorine to free chlorine. No evidence of nitrification was observed during the course of the study.

Keywords: Disinfection By-Products; Distribution System; Trihalomethanes; Haloacetic Acids; Disinfection; Heterotrophic Plate Counts; Nitrification

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CHAPTER 1
INTRODUCTION

Disinfection is an established water treatment process used to inactivate pathogenic microorganisms; however, disinfectants can react with natural organic matter (NOM) to produce disinfection by-products (DBPs) that may cause adverse health effects. Trihalomethanes (THMs) and haloacetic acids (HAAs) have been identified as the primary DBPs, constituting approximately 50% of the total organic halide (TOX) present on a weight basis (Krasner et al, 1989; Stevens et al, 1989; Singer and Chang, 1989). The wide-spread occurrence and chronic health effects associated with DBPs led to the establishment of regulatory limits for THMs and HAAs by the United States Environmental Protection Agency (USEPA; USEPA, 1998). Currently, the Stage 1 Disinfectants and Disinfection By-Products (D/DBP) Rule regulates THMs to a maximum contaminant level (MCL) of 80 μg/L and five of the nine chlorine- and bromine-containing HAAs to a MCL of 60 μg/L measured as a running annual average (RAA) of four quarterly samples collected at four locations in the distribution system for each treatment plant. The recent proposal of the Stage 2 D/DBP Rule attempts to provide equal consumer protection from DBP exposure by using a locational running annual average (LRAA) for regulatory compliance (USEPA, 2003).

Raw water quality, treatment, and distribution system properties affect the chemical, biological, and physical characteristics of tap water. The amount and characteristics of the NOM and its removal prior to the application of a disinfectant influence the extent of DBP formation. Addition of ammonia to free chlorine produces combined chlorine, which often halts the formation of some DBPs. Free chlorine will produce higher concentrations of halogen-containing DBPs than combined chlorine (Wolfe et al, 1984; Johnson and Jensen, 1986; Speitel, 1999; Zhang et al, 2000; Baribeau et al, 2000; Singer, 2001). Therefore, the use of combined chlorine as an alternative secondary disinfectant can significantly decrease the DBP concentrations observed at the tap. As the disinfectant dose and contact time increase, DBP production increases (Stevens et al, 1989; Hooper and Owen, 1994; Singer, 2001). Temperature and pH can also affect the rate and extent of halogenated DBP formation.

Physical, chemical, and biological variations that occur within the distribution system can increase or decrease DBP concentrations from the point of entry into the system to the point of

use. The disinfectant behaves similarly in the distribution system as in the treatment plant with respect to the formation of DBPs; however, the contact time may be considerably longer resulting in increasing THM concentrations as long as a disinfectant residual is maintained (Johnson and Jensen, 1986; Stevens et al, 1989; Reckhow et al, 1990; Meyer et al, 1993; Hooper and Owen, 1994; Singer 1994; Singer et al, 1995; Krasner et al, 1996; Chen and Weisel, 1998; Elshorbagy, 2000; Singer, 2001; Liang and Singer, 2003; Rutledge et al, 2003). Biofilms and corrosion by-products at the pipe wall provide a reservoir of organic material, which exerts a disinfectant demand and results in the continued formation of DBPs (Meyer et al, 1993; Rossman et al, 2001; DiGiano et al, 2002; Rutledge et al, 2003). Biological degradation of HAAs has been observed in full-scale distribution systems at high residence time locations (Williams et al, 1994; Williams et al, 1995; Williams et al, 1996; Lebel et al, 1997; Chen and Weisel, 1998; Williams et al, 1998). Mono- and dihaloacetic acids rapidly decay simultaneously in the presence of HAA-degrading bacteria; however, the trihaloacetic acids are only biodegraded after the other haloacetic acid species have been degraded to low concentrations (Van der Ploeg et al, 1991; Williams et al, 1994; Williams et al, 1995; Lebel et al, 1997; Baribeau et al, 2000; Zhou and Xie, 2002). Several other factors also influence the formation and decay of DBPs in the distribution system, including pipe diameter and pipe material; system configuration, operation, and maintenance; and hydraulic conditions.

Biological regrowth within the distribution system can affect HAA degradation, disinfectant residuals, corrosion rates, and risk of infection from pathogenic microorganisms. The disinfectant type and dose have a substantial effect on microbial regrowth in both the bulk liquid phase and as a biofilm at the pipe wall. Combined chlorine provides a stable disinfectant residual that is effective in controlling biofilm growth; however, chlorine is a much stronger disinfectant and provides better control of regrowth in the bulk liquid phase provided an adequate residual can be maintained (LeChevallier et al, 1988b; LeChevallier et al, 1990; LeChevallier et al, 1996; Norton and LeChevallier, 1997; Speitel, 1999; DiGiano et al, 2000). Attachment effects and temperature also significantly impact the ability of a microbial population to establish a biofilm.

Nitrification can occur in chloraminated distribution systems due to the growth of ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). Increased heterotrophic plate counts (HPCs) and coliform concentrations are some of the adverse effects

associated with nitrification. Typical indicators include a sharp decrease in combined chlorine residual, significant increases in HPCs, and a reduction in ammonia concentrations correlating to increases in nitrite and/or nitrate concentrations (Wilczak et al, 1996; Odell et al, 1996; Lipponen et al, 2002; Pintar et al, 2002; DiGiano et al, 2002). Due to the biological nature of nitrification, increases in temperature and decreases in disinfectant concentration correspond to increased AOB and NOB concentrations (Wilczak et al, 1996; Odell et al, 1996; Pintar et al, 2002). The most common control measure for nitrification, aside from maintaining a persistent disinfectant residual, is the of use break-point chlorination with free chlorine.

The object of this study was to evaluate factors affecting the formation and decay of DBPs in a full-scale distribution system. The sampling was conducted on six dates at 14 points throughout the distribution with varying residence times, pipe diameters, and pipe materials. The utility was required to annually switch from combined chlorine to free chlorine as a secondary disinfectant for one month to control nitrification, allowing for the assessment of DBP formation and disinfectant behavior before, during, and after the switch to free chlorine. The free and total chlorine residual and the four THM and nine HAA species concentrations were measured at all 14 sample locations. The NOM entering the distribution system was quantified using total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UV 254) analyses. Ammonia, nitrite, and nitrate concentrations were assessed to determine if nitrification was occurring. Bacterial regrowth was also monitored during the disinfectant switch.

This work was part of a larger project sponsored by the American Water Works Association Research Foundation (AWWARF), with Carrollo Engineers as the principal contractor. The work was done in cooperation with the University of North Carolina – Chapel Hill (UNC-CH), American Water Works Service Company, Newport News Waterworks, University of Waterloo, and five United States water utilities. The five utilities examined present a wide range of raw water qualities, treatment processes, and distribution system characteristics to evaluate the factors affecting the physical, chemical, and biological changes in water quality in full-scale distribution systems. Sampling and analyses similar to those presented in this report were conducted at all of the utilities over a one-year period, including N-nitrosodimethylamine (NDMA) and bromide analyses at several utilities.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

Disinfection has a long history of use in public water supplies for the inactivation of pathogenic microorganisms to protect the health of the consuming population; however, in the 1970's disinfection by-products (DBPs) were identified and associated with adverse health effects. Since that time, the United States Environmental Protection Agency (USEPA) has worked to balance the health risks of microbial pathogens and DBPs through regulatory measures. DBPs are formed by the reaction of disinfectants with natural organic matter (NOM), and their concentration is affected by numerous water quality, treatment, and distribution system characteristics. Secondary disinfection is used in the distribution system for the control of microbial regrowth in both the liquid phase and as a biofilm on the pipe wall.

2.2 DISINFECTANT CHEMISTRY

Disinfection has been used widely in the United States since the early 1900's for inactivation of pathogenic microorganisms. Some common disinfectants in water treatment include free chlorine, combined chlorine, ozone, chlorine dioxide, and ultraviolet radiation. Primary disinfectants are used within the treatment plant at a particular dose and contact time to achieve microbial inactivation. Once the treated water leaves the plant, a secondary disinfectant is used to control microbial regrowth within the distribution system.

2.2.1 Chlorine

Chlorine is the most commonly used primary and secondary disinfectant, and can be applied as gaseous chlorine, liquid sodium hypochlorite, or solid calcium hypochlorite. When chlorine gas is added to water, a rapid hydrolysis occurs in which hypochlorous acid (HOCl) is formed, as illustrated in Equation 2.1

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2.1)$$

Hypochlorous acid maintains equilibrium with hypochlorite (OCl^-) via a dissociation reaction depending on pH, as illustrated in Equation 2.2. The acidity constant of hypochlorous acid at room temperature is approximately $10^{-7.6}$ (Haas, 1999).

$$HOCl \rightarrow OCl^- + H^+ \quad (2.2)$$

Hypochlorous acid is a more effective disinfectant than hypochlorite; therefore, disinfection efficacy increases with decreasing pH for a given set of conditions.

2.2.2 Combined Chlorine

Combined chlorine, also referred to as chloramines, is used primarily as a secondary disinfectant, and is produced by the addition of chlorine and ammonia to treated water to form monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3) in a stepwise manner as seen in Equations 2.3, 2.4, and 2.5.

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O \quad (2.3)$$
$$HOCl + NH_2Cl \leftrightarrow NHCl_2 + H_2O \quad (2.4)$$
$$HOCl + NHCl_2 \leftrightarrow NCl_3 + H_2O \quad (2.5)$$

The extent to which each combined chlorine species is formed depends on the chlorine to ammonia ratio and the solution pH. The sum of the three chloramine species concentrations is referred to as combined chlorine; however, monochloramine is the predominant and the most desirable species formed under most water treatment conditions (Wolfe, 1984). The production of monochloramine at a chlorine to ammonia ratio of 5:1 on a mg/mg weight basis (1:1 molar ratio) is stoichiometrically optimal; however, any increase above the 3:1 chorine to ammonia ratio can result in a loss in the combined chlorine residual due to breakpoint chlorination reactions (Symons et al, 1998; Vikesland et al, 2001). Some utilities prefer to reduce the chlorine to ammonia ratio to as low as 3:1 on a mg/mg weight basis to avoid this loss in combined

chlorine residual; however, the decreased chlorine to ammonia ratio results in excess ammonia availability in the distribution system, which promotes nitrification.

Monochloramine can decompose by hydrolysis and general acid catalyzed disproportionation to form dichloramine (Vikesland et al, 1998; Speitel, 1999; Vikesland et al, 2001). Dichloramine formation is dependent on water quality characteristics including pH, temperature, and alkalinity. Once dichloramine has formed, a series of rapid redox reactions produce ammonia, chloride, nitrogen gas, and nitrate. Monochloramine is most stable at pH values between 8 and 8.5 and at low temperatures (Symons et al, 1998; Vikesland et al, 2001).

2.3 DISINFECTION BY-PRODUCTS

Due to the adverse health effects associated with DBP exposure, the USEPA has established maximum contaminant levels (MCLs) for some DBPs. The MCLs have been lowered as analytical capabilities have improved and the health effects of specific DBP species are better understood. The concentration and type of DBPs produced depend on raw water characteristics, treatment processes used, and distribution system characteristics.

2.3.1 Regulatory Aspects

The simultaneous discovery of trihalomethanes (THMs) in drinking water by Rook (1974) and Bellar and Lichtenberg (1974) coincided with the identification and classification of chloroform as a carcinogen (National Cancer Institute, 1976), which has ultimately led to the regulation of DBPs by the USEPA (1979). Since the initial identification of THMs, additional classes of DBPs have been measured in drinking water including haloacetic acids (HAAs), haloketones, haloacetonitriles, cyanogen halides, oxyhalides, aldehydes, and aldo and ketoacids. The aggregate concentration of all organo-halogenated DBPs is represented by the total organic halide (TOX) concentration; however, less than half of the chemicals contributing to the TOX concentration have been identified (Singer and Chang, 1989).

2.3.1.1 Health Effects

A continually growing body of epidemiological research has established links between DBP exposure and adverse cancer and reproductive health effects. Increased risk of bladder, colon, and rectal cancer is weakly associated with chronic exposure to chlorinated drinking water in epidemiological and clinical studies (Morris et al, 1992; Cantor et al, 1998; Hildesheim et al, 1998; Calderon, 2000). Increased risks of liver and kidney cancer have been established in experimental animals; however, human studies have not replicated these results (Herren-Freund et al, 1987; Bull, 2001). DBPs have also been associated with adverse reproductive and developmental health effects including spontaneous abortion, low birth weight, birth defects, prematurity, and intrauterine growth retardation due to acute exposure (Bove et al, 1995; Savitz et al, 1995; Waller et al, 1998; Klotz and Pyrch, 1999; Dodds et al, 1999; Calderon, 2000). Recently, Kargalioglu et al (2000) observed that the cytotoxic and mutagenic effects of the brominated THM and HAA species were more severe then the chlorinated species.

The primary source of THM exposure is via drinking water, where routes of exposure include ingestion, inhalation, and percutaneous uptake (Dijk-Looijaard and Genderen, 2000). Water use activities that involve inhalation and dermal exposure result in higher concentrations of THMs in the blood then activities limited to ingestion exposure (Backer et al, 2000; Miles et al, 2002; Singer et al, 2003). THM concentrations in indoor air are also significantly higher as a result of water use activities in which volatilization is more probable, and correspond well with concentrations in tap water and blood (Singer et al, 2003). The concentration of THMs in the blood is proportional to the concentration in the tap water; however the concentration in blood is three orders of magnitude lower than the concentration in the tap water (Miles et al, 2002). Additionally, the distribution of THM species in the blood is similar to the speciation in the tap water (Miles et al, 2002; Singer et al, 2003).

2.3.1.2 Regulations

The wide-spread occurrence and adverse health effects associated with DBPs have led to their regulation in finished drinking water. The USEPA (1979a) established the Interim Trihalomethane Rule in 1979, which regulated the four species of THMs (THM4): chloroform

($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$) as a group with an MCL of 100 µg/L. This concentration was regulated as the running annual average of four quarterly samples collected at four locations in the distribution system for each treatment plant. The rule applied to all community water systems serving at least 10,000 people that employed a disinfectant during any part of the treatment process. Utilities serving less than 10,000 people were not included in the rule because of concerns regarding the possible contamination of water supplies with pathogenic microorganisms (Singer, 1994; Pontius, 1999). The regulation was established for the THM4 class as a whole instead of for the individual THM species because the adverse health effects associated with each species were not well quantified (Singer et al, 1994).

After a regulatory negotiating procedure, the Stage 1 Disinfectants and Disinfection By-Products (D/DBP) Rule was promulgated in November 1998, reducing the THM4 MCL to 80 µg/L and establishing an MCL of 60 µg/L for a group of five haloacetic acids (HAA5): monochloroacetic acid (ClAA), monobromoacetic acid (BrAA), dichloroacetic acid (Cl_2AA), dibromoacetic acid (Br_2AA), and trichloroacetic acid (Cl_3AA) (USEPA, 1998; Pontius, 1999). The concentration of each class of DBPs was again regulated as a running average of four quarterly samples collected at four locations in the distribution system for each treatment plant. In addition, the rule established maximum residual disinfectant levels (MRDLs) of 4 mg/L for both free chlorine and combined chlorine disinfection regulated as an annual average. The Stage 1 D/DBP Rule applies to all community water systems that apply a disinfectant to drinking water, regardless of the community population served.

Most recently the Stage 2 D/DBP Rule has been proposed to ensure equal consumer protection from DBP exposure (USEPA, 2003). This rule consists of an initial distribution system evaluation (IDSE), an alteration in the compliance paradigm for annual average DBP concentrations, and monitoring of peak DBP concentrations. The IDSE will be used to determine the locations of the highest THM4 and HAA5 concentrations within the distribution system. To ensure equal consumer protection, the locational running annual average (LRAA) will replace the existing system-wide annual average for regulatory compliance by averaging the quarterly THM4 and HAA5 concentrations for each sampling location on an annual basis. Utilities will also be required to monitor and reduce "significant excursions" that occur as short-term peaks in DBP concentrations to limit acute exposure. One substantial concern not addressed by the Stage

2 D/DBP Rule is the lack of regulation of four of the nine bromine- and chlorine-containing HAA species (bromochloroacetic acid (BrClAA), bromodichloroacetic acid ($BrCl_2AA$), dibromochloroacetic acid (Br_2ClAA), tribromoacetic acid (Br_3AA)), which are not currently included in the MCL for HAA5. Researchers have found significant concentrations of the unregulated HAAs, and have recommended that these HAAs should be included in future regulations (Cowman and Singer, 1996; Roberts et al, 2002).

2.3.2 Water Quality and Treatment Characteristics

The raw water quality characteristics and treatment processes used by a utility significantly affect the extent and speciation of DBPs formed prior to entry into the distribution system. The concentration and chemical characteristics of NOM; disinfectant type, concentration, and contact time; temperature; pH; and bromide concentration greatly influence DBP formation.

NOM is a heterogeneous mixture of organic material with high and low molecular weight, organic acids and varying degrees of hydrophobicity and aromaticity. The chemical characteristics of NOM are influenced by the source material and biogeochemical processes that occur during its formation. NOM can be classified operationally as hydrophilic, transphilic, and hydrophobic depending on its affinity for water. The hydrophobic fraction consists of high molecular weight acids and can be further classified as humic, which are less soluble, or fulvic, which are more soluble acids. Surrogate measures of NOM include total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet absorbance at a wavelength of 254 nm (UV 254) (Owens et al, 1995; Croue et al, 1999; Wu et al, 2000).

All fractions of NOM are reactive with chlorine to varying degrees to form DBPs; however, THM4 and HAA9 have distinct formation mechanisms and/or organic precursors (Symons et al, 1998; Croue, 1999; Singer and Liang, 2003). In general, higher concentrations of NOM and more hydrophobic NOM result in increased formation of DBPs (Krasner et al, 1989; Reckhow et al, 1990; Singer, 1994; Singer et al, 1995; Krasner et al, 1996; Arora et al, 1997; Croue et al, 1999; Gallard and Guten, 2001; Rossman et al, 2001). Hydrophobic acids are the primary DBP precursors, where humic acids are more reactive than fulvic acids (Peters et al, 1980; Reckhow et al, 1990; Croue et al, 1999; Liang and Singer, 2003). Reckhow et al (1990)

also found that chlorine demand was higher for humic acids relative to fulvic acids. The hydrophilic fraction of NOM may be more important in the formation of THM4 in low humic acid-containing waters (Reckhow et al, 1990; Croue et al, 1999). Additionally, the kinetic rate of formation of DBPs can be significantly affected by the nature of the organic material (Croue et al, 1999; Gallard and Guten, 2001). HAA9 will form more quickly, predominantly in the treatment plant, while THM4 formation occurs in the treatment plant and will continue to form to a significant degree in the distribution system (Rook, 1977; Singer 2001; Gallard and Guten, 2001).

Disinfectant type, concentration, and contact time influence the rate and distribution of DBP species. Chlorine can react with organic matter by oxidation of reduced components, addition to unsaturated sites, and substitution into the organic matrix, where the latter reactions result in the formation of halogenated DBPs (Johnson and Jensen, 1986; Vikesland et al, 1998; Speitel, 1999). Free chlorine has a greater tendency to participate in substitution reactions than monochloramine; therefore, chlorine disinfection will produce higher concentrations of halogen-containing DBPs than chloramination (Wolfe et al, 1984; Johnson and Jensen, 1986; Norton and LeChevallier, 1997; Speitel, 1999; Zhang et al, 2000; Baribeau et al, 2000; Singer, 2001). The organic demand for combined chlorine is much less than that for free chlorine; however, small concentrations of free chlorine are present during chloramination, resulting in small increases in DBP concentrations (Johnson and Jensen, 1986; Speitel, 1999). Lower chlorine to ammonia ratios result in increased stability of combined chlorine and decreased DBP formation (Symons et al, 1998). Regardless of the disinfectant used, higher disinfectant doses increase the reaction kinetics and extent of DBP formation, resulting in increased DBP concentrations (Stevens et al, 1989; Hooper and Owen, 1994; Singer, 1994; Singer, 2001). In addition, DBP formation will continue with increasing contact time as long as a disinfectant residual persists.

Temperature and pH can affect the rate and extent of halogenated DBP formation. Temperature affects the rate of reaction of disinfectants with NOM, where increased temperatures result in faster reaction kinetics. The increase in chlorine reaction kinetics requires increased application of the disinfectant to achieve specific disinfection requirements, thereby producing higher concentrations of DBPs at higher temperatures (Peters et al, 1980; Krasner et al, 1989; Singer, 1994; Hooper and Owen, 1994; Singer et al, 1995; Krasner et al, 1996; Arora et al, 1997; Lebel et al, 1997; Chen and Weisel, 1998; Baribeau et al, 2000; Singer, 2001). The

chlorine-substituted DBPs are more sensitive to temperature change than the bromine-substituted species due to the slower formation kinetics of the chlorine-substituted species (Hooper and Owen, 1994; Krasner et al, 1996). THM4 formation increases with increasing pH, while trihaloacetic acid (X_3AA) formation increases with decreasing pH, over the pH range used during most water treatment conditions (Rook, 1977; Peters et al, 1980; Johnson and Jensen, 1986; Stevens et al, 1989; Krasner et al, 1989; Reckhow et al, 1990; Hooper and Owen, 1994; Symons et al, 1998; Wu et al, 2000; Singer, 2001; Liang and Singer, 2003). Monohaloacetic acids (XAA) and dihaloacetic acids (X_2AA) are unaffected by changes in pH (Stevens et al, 1989; Reckhow et al, 1990; Singer, 2001; Liang and Singer, 2003)

The concentration of bromide present in the raw water has a substantial effect on the speciation of the DBPs produced; however, increased bromide concentration results in little or no increase in the overall concentration of DBPs (Symons et al, 1998; Zhang et al, 2000; Wu et al, 2000). Hypochlorous acid reacts with bromide to produce hypobromous acid, which goes on to react with NOM to produce brominated DBPs (Singer, 1994). Bromine is more reactive than chlorine in substitution and addition reactions; therefore, brominated species will form more quickly than chlorinated species (Hooper and Owen, 1994; Cowman and Singer, 1996; Krasner et al, 1996). The chlorine to bromide ratio is dependent on the disinfectant concentration applied, which in turn relates to the organic matter removed during treatment (Arora et al, 1997). As the chlorine to bromide ratio is decreased, a shift in the speciation of DBPs toward more brominated and mixed chlorobromo species will occur (Krasner et al, 1989; Singer, 1994; Cowman and Singer, 1996; Arora et al, 1997; Symons et al, 1998).

2.3.3 Distribution System Characteristics

The physical, chemical, and biological attributes of the distribution system affect the continued formation and decay of DBPs in the distribution system. Physical and chemical variations that occur within the distribution system can increase concentrations of DBPs from the point of entry into the distribution system to the point of use. These changes include: the secondary disinfectant type, concentration, and contact time; pipe material and diameter; distribution system configuration, operation, and maintenance; hydraulic conditions; and

temperature. Biological growth within the distribution system can cause the degradation of some DBPs.

2.3.3.1 Secondary Disinfectant Type, Concentration, and Contact Time

Disinfectant type, concentration, and contact time affect the continued formation of DBPs in the distribution system. Secondary disinfection by free chlorine will result in the formation of higher concentrations of THMs and HAAs compared to combined chlorine disinfection, although the formation of dihaloacetic acids (X_2AA) are not as well controlled by chloramination as other DBPs (Wolfe et al, 1984; Johnson and Jensen, 1986; Stevens, 1989; Singer, 1996; Speitel, 1999; Cowman and Baribeau et al, 2000; Zhang et al, 2000). Zhang et al (2000) observed THM4 concentrations less than 10 µg/L and HAA9 concentrations less than 35 µg/L in a model water with a combined chlorine dose of 5.0 mg/L as Cl_2, while a THM4 concentration of 250 µg/L and an HAA9 concentration of approximately 120 µg/L were observed in the same model water for a chlorine dose of 4.5 mg/L as Cl_2. Dichloroacetic acid constituted more than 90% of the HAA9 concentration by weight in the study conducted by Zhang et al (2000). Cowman and Singer (1996) found HAA9 production was decreased by 90 to 95% when chloramination was used for disinfection instead of free chlorine. Combined chlorine is often used as an alternative disinfectant because of the sharp decreases in DBP formation when compared to free chlorine.

A disinfectant dose that will maintain a residual throughout the distribution system is required at the point of entry. However, free chlorine and combined chlorine decay at different rates throughout the distribution system as reactions with organic chemicals, inorganic chemicals, and biofilms occur (Meyer et al, 1993; Krasner et al, 1996; Chen and Weisel, 1998; Baribeau et al, 2001; Liang and Singer, 2003). Increases in the disinfectant dose result in increases in DBP concentrations, where the chloro-substituted species account for the majority of the increase in DBP concentration (Hooper and Owen, 1994; Elshorbagy, 2000).

The contact time between a secondary disinfectant and treated water is a complex function of the distribution system network design, water demand patterns, storage volume and operation of the storage tanks (Singer, 2001). Increases in contact time result in increased DBP formation as long as a disinfectant residual persists (Johnson and Jensen, 1986; Stevens et al, 1989; Reckhow et al, 1990; Meyer et al, 1993; Hooper and Owen, 1994; Singer 1994; Singer et

al, 1995; Krasner et al, 1996; Chen and Weisel, 1998; Elshorbagy, 2000; Singer, 2001; Liang and Singer, 2003; Rutledge et al, 2003). HAA9 and THM4 formation are characterized by a fast initial rate of reaction followed by continued formation at a slower rate. However, the reaction kinetics of HAA9 are much faster than those of THM4, causing the majority of HAA9 formation to occur immediately after the disinfectant is applied (Singer, 2001; Gallard and Guten, 2001, Liang and Singer, 2003). In addition, tribromo-, dibromochloro-, and bromodichloroacetic acid species can degrade to their corresponding THM species within the distribution system under normal temperature and pH conditions, increasing THM4 concentrations in the distribution system at the expense of HAA9 (Zhang and Minear, 2002). Diurnal variation in DBP concentrations greater than 50% have been observed by Singer and Kachur (1995) due to changes in contact time as a result of fluctuations in demand.

2.3.3.2 Pipe Material and Pipe Diameter

The distribution system pipe material and pipe diameter can affect DBP concentrations through disinfectant reactions with biofilms and corrosion by-products at the pipe wall. Biological growth in the distribution system, the pipe material, and corrosion by-products exert a disinfectant demand, requiring an increased disinfectant dose at the point of entry into the distribution system (Meyer et al, 1993; DiGiano et al, 2002; Rutledge et al, 2003). The biofilm and corrosion by-products provide a reservoir of organic and inorganic material with which the secondary disinfectant can react, increasing DBP concentrations (LeChevallier et al, 1996; Rossman et al, 2001). DBP production due to reactions between the organic material at the pipe wall and the secondary disinfectant can be limited by the rate of mass transfer of the disinfectant between the bulk phase and the pipe wall (Vasconcelos et al, 1997).

DBP production is greater in full-scale distribution systems than in batch tests that simulate bulk-phase demand, even when the same disinfectant type, dose, and contact time are used because pipe walls, corrosion by-products, and biofilms can continue to react with the secondary disinfectant (Meyer et al, 1993; Rossman et al, 2001; Baribeau et al, 2001). Rossman et al (2001) found THM4 concentrations were 15% higher in a simulated distribution system than in parallel batch experiments; however, they saw no differences in HAA6 concentrations. In addition, they noted that the first-order reaction rate for the loss of free chlorine at the pipe wall

due to biofilm and corrosion by-product demand was an order of magnitude higher than the corresponding rate for the loss of chlorine in the bulk phase (Rossman et al, 2001). Others have observed that the chlorine demand of corrosion by-products were more significant than the chlorine demand of the biofilm (Kiene et al, 1999; Baribeau et al, 2001).

Disinfectant decay due to interactions with corrosion by-products is limited by the dissolution of the corrosion by-products into the bulk liquid phase (Kiene et al, 1999). Corrosion by-products are formed as a result of a series of electrochemical reactions at a metal pipe wall surface in contact with an electrolyte-containing liquid phase. Increased corrosion rates result in a decrease in secondary disinfectant efficacy, where free chlorine is more dramatically affected than combined chlorine (LeChevallier et al, 1990; LeChevallier et al, 1993; Rutledge et al, 2003). Corrosion rates are elevated as temperature increases, thereby increasing the availability of organic and inorganic material with which secondary disinfectants can react (LeChevallier et al, 1996; Norton and LeChevallier, 1997; Rutledge et al, 2003).

Disinfectant decay is more pronounced as the surface area to volume ratio in the pipe increases, resulting in increased disinfectant decay in smaller diameter pipes (Vasconcelos et al, 1997; Prevost et al, 1998; Lu et al, 1999; Baribeau et al, 2001). Tubercles on iron pipes can also increase the internal surface area throughout the distribution system, increasing the disinfectant demand (LeChevallier et al, 1996). Prevost et al (1998) found that surface area to volume ratios were important for residence times less than nine hours in a full-scale distribution system. However, at residence times more than nine hours the effect was insignificant because the treated water had traveled through large diameter pipes to get to smaller diameter pipes, where the water was rapidly used. Others have found that surface area to volume ratios only affected chlorine demand in pipes smaller than 80 mm in diameter (Lu et al, 1999; Kienen et al, 1999).

2.3.3.3 Biodegradation of HAA9

Biological degradation of HAA9 was first observed on a laboratory scale; however, decreasing HAA9 concentrations have subsequently been observed at high residence times in full-scale distribution systems (Van der Ploeg et al, 1991; Singer et al, 1993; Williams et al, 1994; Williams et al, 1995; Williams et al, 1996; Lebel et al, 1997; Williams et al 1998; Chen and Weisel, 1998; Baribeau et al, 2000). Several bacteria have been isolated that are capable of

HAA degradation. *Xanthobacter autotrophicus GJ10* has been the subject of several studies due to its ability to degrade the mono and dihaloacetic acids (Van der Ploeg et al, 1991; Williams et al, 1996; Williams et al, 1998). *GJ10* can utilize multiple HAA species as a substrate, and most effectively degrades the dihaloacetic acids (Van der Ploeg et al, 1991; Williams et al, 1996). Williams et al (1995, 1996) have also isolated several types of bacteria from the Newport News, VA water distribution system that readily biodegrade HAA9. One type of bacteria was able to degrade all HAA9 species effectively; however, the degradation occurred at a slower rate when compared to other HAA-degrading bacteria from the distribution system (Williams et al, 1996). The enzymatic haloacid dehalogenization process used by HAA9-degrading bacteria results in an increase in chloride ion concentration and a decrease in pH (Van der Ploeg et al, 1991; Williams et al, 1995; Williams et al, 1996).

In both laboratory and full-scale studies, the mono and dihaloacetic acids have been found to rapidly decay simultaneously in the presence of HAA9-degrading bacteria; however, trihaloacetic acid (X_3AA) degradation has consistently lagged until the other species are depleted to low concentrations (Van der Ploeg et al, 1991; Williams et al, 1994; Williams et al, 1995; Lebel et al, 1997; Chen and Weisel, 1998; Baribeau et al, 2000; Zhou and Xie, 2002). Therefore, the higher the number of halogenated atoms on a haloacetic acid molecule, the slower the biodegradation rate (Zhou and Xie, 2002). Several utilities have observed decreases in HAA9 concentrations at high residence times within the distribution system, while THM4 concentrations consistently increased with increasing residence time (Williams et al, 1994; Williams et al, 1995; Williams et al, 1996; Chen and Weisel, 1998). The locations at which HAA9 degradation was occurring corresponded to low disinfectant residuals and high heterotrophic plate counts (HPCs) (Williams et al, 1994). In addition, HAA9 degradation was more severe during warm weather months (Williams et al, 1994; Chen and Weisel, 1998; Baribeau et al, 2000). In subsequent laboratory experiments, HAA9 degradation was observed to correlate well with increases in HPC concentrations (Williams et al, 1994).

Biologically activated carbon (BAC) has been suggested as a possible treatment technology to reduce the concentration of HAA9 prior to entry into the distribution system. Arora et al (1997) found HAA5 concentrations decreased by 70% due to adsorption and biodegradation through a BAC filter, where increased rates of degradation were observed during the summer months. Xie and Zhou (2002) observed HAA5 to be completely degraded during a

7-hour filter run through BAC, except for a small concentration of Cl_3AA that remained. During an extended study, they found that the monohaloacetic acids (XAA) developed a biologically degrading community first, followed by the di- and trihaloacetic acids, respectively (Xie and Zhou, 2002).

2.4 BACTERIAL REGROWTH WITHIN THE DISTRIBUTION SYSTEM

Biological regrowth within the distribution system, in both the bulk liquid phase and as a biofilm on the pipe wall, can result in increased disinfectant demand, corrosion rates, risk of gastroenteritis, and customer complaints due to taste, odor, and the presence of particles. The choice of disinfectant and the dose at which it is applied have a substantial effect on microbial regrowth within the distribution system. Combined chlorine disinfection provides a stable residual that is effective in controlling biofilm growth; however, it is a weak disinfectant. Free chlorine is a much stronger disinfectant and is therefore better able to control microbial growth in the bulk liquid phase; however, because it is a stronger oxidant, it will participate in more reactions with the pipe wall material, corrosion by-products, and biological constituents causing a continually declining residual with increasing residence time in the distribution system (Wolfe et al, 1984; Johnson and Jensen, 1986; LeChevallier et al, 1988b; LeChevallier et al, 1990; LeChevallier et al, 1996; Norton and LeChevallier, 1997; Speitel, 1999; DiGiano et al, 2000).

Combined chlorine is better able to penetrate and disinfect the biofilm because of the limited reactions that occur with other demand-causing compounds (LeChevallier et al, 1988b; LeChevallier et al, 1993). In full-scale distribution systems, a minimum residual of 0.5 mg/L of free chlorine or 1 mg/L of combined chlorine must be maintained to control microbial growth (LeChevallier et al, 1996; Momba et al, 2003). LeChevallier et al (1990) found a monochloramine dose of 2 mg/L was required to effectively control biofilm growth on iron pipe, where chlorine doses up to 4 mg/L were ineffective. Chlorine and combined chlorine doses of 1 mg/L were effective in controlling biofilm growth on galvanized iron, copper, and PVC pipes. Similar bacterial populations were resistant to disinfection by free chlorine and combined chlorine on all pipe materials. In a later study examining 31 full-scale distribution systems, LeChevallier et al (1996) found the density of coliform bacteria was 35 times higher in chlorinated systems than in chloraminated systems.

Increased corrosion rates can correspond to increases in microbial concentrations (LeChevallier et al, 1996). Combined chlorine is a more effective disinfectant in corrosive environments; however, free chlorine can be an effective secondary disinfectant in moderate to low corrosive environments (LeChevallier et al, 1993). Phosphate additives, often used for corrosion control, can significantly decrease biofilm concentrations, which result in a reduction in the oxidant demand of the disinfectant (LeChevallier et al, 1990; LeChevallier et al, 1996).

Some utilities using combined chlorine as a secondary disinfectant switch to free chlorine for a period of time to limit ammonia-oxidizing bacteria and nitrite-oxidizing bacteria growth within the distribution system; however, this can result in increased HPC and coliform concentrations. LeChevallier et al (1990) found that switching from a 4 mg/L dose of free chlorine to the same dose of combined chlorine resulted in a three-fold decrease in biofilm bacterial concentrations in the laboratory. In a subsequent full-scale study, switching from free chlorine to combined chlorine resulted in a 50% decrease in coliform incidence (LeChevallier et al, 1996). Additional full-scale research showed HPC concentrations decreased by an order of magnitude when the secondary disinfectant was switched from free chlorine to combined chlorine; however, HPC concentrations rose to pre-chloramination levels after switching back to free chlorine (Norton and LeChevallier, 1997). Momba et al (2003) also observed dramatic decreases in HPC concentrations when a 2.5 mg/L chlorine dose was replaced by a 1.5 mg/L combined chlorine dose. DiGiano et al (2002) found HPCs quickly returned to pre-chlorine levels after returning to combined chlorine disinfection in a full-scale distribution system.

Several additional factors can affect the ability of a microbial population to establish a biofilm including attachment effects, temperature effects, and residence time. Microbial attachment to the pipe surface provides protection from both hydraulic sloughing and disinfectant penetration (LeChevallier et al, 1988a; LeChevallier et al, 1990; LeChevallier et al, 1996). Colonized surfaces are more resistant to chlorine disinfection; however, bacterial colonization has little effect on the ability of combined chlorine to inactivate microbial populations at the pipe wall (LeChevallier et al, 1988a). LeChevallier et al (1988a) observed a 150-fold increase in resistivity to free chlorine when bacteria were attached to a surface, while resistivity to combined chlorine disinfection was only increased by two-fold. Bacterial concentrations increase in the distribution system with increasing temperature and residence time, most likely as a result of corresponding decreases in secondary disinfectant concentrations

under these conditions (Colbourne et al, 1991; LeChevallier et al, 1996; Prevost et al, 1998; Lu et al, 1999; Baribeau et al, 2000; DiGiano et al, 2001).

2.5 NITRIFICATION IN THE DISTRIBUTION SYSTEM

Nitrification can occur in chloraminated distribution systems due to the growth of ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). Typical indicators of a nitrification incidence include a sharp decrease in the combined chlorine residual, severe increases in HPCs, a reduction in ammonia concentrations correlating to increases in nitrite and/or nitrate concentrations, and, in some cases, a decrease in pH and dissolved oxygen (Wilczak et al, 1996; Odell et al, 1996; Lipponen et al, 2002; Pintar et al, 2002; DiGiano et al, 2002). Nitrite concentrations increase by 0.05 to 0.5 mg/L during a nitrification incidence, and follow the same general trend as AOB concentrations (Odell et al, 1996; Lipponen et al, 2002; Pintar et al, 2002). A prolonged nitrification event is characterized by a decrease in ammonia concentration through the distribution system combined with an increase in nitrate concentration, while there is no change in the nitrite concentration (Wilczak et al, 1996).

AOB and NOB populations within drinking water distribution systems have not been well characterized, but the general phylogeny of the bacteria and growth rate comparisons are available. Common genera of AOB are *Nitrosomonas* and *Nitrosospira*, and common genera of NOB include *Nitrobacter* and *Nitrospira* (Regan et al, 2002). Biological ammonia oxidation has a higher energy yield than nitrite oxidation; therefore, AOB may be present in higher concentrations than NOB (Lipponen et al, 2002).

Due to the biological nature of nitrification within the distribution system, increases in temperature correspond to increased AOB and NOB concentrations for a given disinfectant dose (Wilczak et al, 1996; Odell et al, 1996; Pintar et al, 2002). Although most nitrification episodes occur at temperatures above 15°C, AOB and NOB populations have developed in distribution systems in waters below 5°C (Wilczak et al, 1996; Lipponen et al, 2002). Pintar et al (2002) observed AOB and NOB populations to be established at the same time regardless of temperature; however, the population that developed at 22°C was one to two orders of magnitude higher in concentration than the population developed at 12°C.

While a high combined chlorine dose discourages AOB and NOB growth, these microorganisms have developed active communities in locations where significant combined chlorine residuals persist in the distribution system (Wilczak et al, 1996; Odell et al, 1996; Regan et al, 2002). A combined chlorine residual of 1 mg/L is required throughout the distribution system to prevent the development of AOB and NOB within the biofilm at approximately 15°C; however, combined chlorine concentrations as high as 2 mg/L are required for temperatures of 25°C (Odell et al, 1996). In a survey of 40 US utilities, Wilczak et al (1996) found AOB and NOB populations were able to survive and proliferate in warm waters at combined chlorine concentrations up to 1.5 mg/L. The risk of developing AOB and NOB populations within the distribution system is increased as the chlorine to ammonia ratio is decreased; however, high chlorine to ammonia ratios cannot eliminate the possibility of a nitrification episode (Odell et al, 1996). Some studies have shown that higher residence time locations are at increased risk of nitrification occurrence because of the low disinfectant residuals often observed at maximum residence time locations (Odell et al, 1996; Lipponen et al, 2002; DiGiano et al, 2002).

Several common control measures have been utilized by utilities to recover from a nitrification occurrence within the distribution system, including break-point chlorination, improved removal of organic matter, increased combined chlorine residuals, decreased residence times, and physical cleaning of the distribution system (Odell et al, 1996). Break-point chlorination of the distribution system is an effective method to remediate a nitrification incidence; however, there are several drawbacks including high DBP production, increased taste and odor complaints, and possible coliform and HPC violations (Wilczak et al, 1996; Odell et al, 1996). Some utilities use break-point chlorination for a period of time during the year to prevent nitrification within the distribution system, but this practice provides little or no long-term benefit (Odell et al, 1996). Pintar et al (2002) observed AOB and nitrite concentrations to return to pre-chlorine levels within two weeks of switching back to combined chlorine as a secondary disinfectant in a bench-scale study. Once a nitrification incident has occurred, increasing the combined chlorine concentration will not reestablish a significant disinfectant residual; therefore, increasing combined chlorine concentrations is an ineffective method of controlling nitrification in the distribution system once an episode has occurred (Odell et al, 1996; Pintar et al, 2002).

CHAPTER 3
MATERIALS AND METHODS

3.1 INTRODUCTION

This study examined changes in water quality from treatment facilities and throughout the distribution system before, during, and after a one-month switch from combined chlorine to free chlorine and then back to combined chlorine. An appropriate utility was selected and sampling sites with varying characteristics were chosen using a hydraulic model of the distribution system and previously obtained information from other researchers and utility employees. The distribution system was sampled twice during each phase of the free chlorine switch. On-site analyses were conducted for total chlorine, free chlorine, and temperature, while heterotrophic plate counts (HPCs), assimilable organic carbon (AOC), free ammonia, nitrite, nitrate, ultraviolet (UV) absorbance, total organic carbon (TOC), trihalomethanes (THM4), and haloacetic acids (HAA9) were analyzed in off-site laboratory facilities. The qualities of all chemical reagents used in the analyses conducted during this study were ACS-grade or better.

3.2 UTILITY SELECTION

The utility selection criteria were based on knowledge of the distribution system, source water characteristics, disinfection by-product (DBP) concentrations, and disinfection practices. The utilities considered were required to have a recently calibrated hydraulic model of the distribution system that could be analyzed to determine optimal sampling locations based on residence times and pipe characteristics. A non-blended (groundwater or surface water) raw water source was preferred to reduce the complexity of identifying the causes of DBP formation and degradation. DBP concentrations of more than 40 µg/L of THM4 and 20 µg/L of HAA9 were essential to observe significant changes in DBP characteristics throughout the distribution system. The final criterion was the changing of disinfectants from combined chlorine to free chlorine and then back to combined chlorine.

Utility A met all of the above criteria, serving a population of approximately 190,000 people through two treatment facilities and producing an annual average total flow of 32 MGD.

Both treatment facilities use the same blended raw water from two lakes, which is treated by the conventional surface water treatment processes of coagulation, flocculation, sedimentation, and filtration. Free chlorine is added to the treated water after sedimentation, and ammonia is added at the point of entry into the distribution system.

The target chlorine to ammonia ratio entering the distribution system is between 3.5:1 and 4:1 on a weight basis for both water treatment plants. Utility A initiated secondary disinfection with combined chlorine in late January, 2002; therefore, the first season of switching from combined chlorine to free chlorine was used during this study. The hydraulic model was developed by Pitometer (Greensboro, NC), and calibrated using flow measurements in the distribution system during the summer of 2002. Zinc orthophosphate is used for corrosion control in the distribution system with an average phosphate residual from 0.3 to 0.35 mg/L. The distribution system consists of two pressure zones with four elevated tanks located throughout the city. The downtown area contains lined and unlined cast iron pipes, while the surrounding area has newer ductile iron pipes.

3.3 SAMPLE SITE SELECTION

A hydraulic model of Utility A's distribution system, in combination with sampling site criteria based on residence time, pipe material, pipe diameter, and known problem areas, were used to identify the most desirable sampling sites. These sites were determined using a matrix of parameters, followed by analysis of the hydraulic model in EPANET version 2.0 (USEPA, 2002) to determine a list of possible sites (Speight, 2002). The model was run using the average daily demand during the summer of 2000, with diurnal variations in demand, for a one-week period. The diameter, length, roughness coefficient, and elevation were entered into the model for each section of pipe. The pump curves, speed, and efficiency were input to the model for the pumps at both treatment plants. The storage tanks in the distribution system had minimum and maximum volume levels and were modeled as completely mixed reactors.

The range of estimated residence times were determined by evaluating the model under the minimum, average, and maximum conditions of diurnal demand on the fourth day of the week. After compiling a list of sites meeting the site selection criteria, Utility A's staff reviewed and approved the sites based on their extensive knowledge of the distribution system. On-site

feasibility of using the proposed sample locations was evaluated by asking water customers if sampling could be conducted at their residence or place of business. Fourteen sample locations were subsequently selected including the two point of entry locations.

3.4 SAMPLE COLLECTION AND HANDLING

Sample bottles for HPC and AOC analyses were provided and shipped by the American Water Works Service Company's (AWWSC) Quality Control and Research Laboratory in Belleville, IL to the Water and Wastewater Research Center (WWRC) in Chapel Hill, NC via Federal Express prior to the sampling date. Sample bottles for chloride, free ammonia, nitrite, and nitrate analysis were prepared at Utility A's analytical laboratory, and picked up prior to sampling. Sample bottles for pH, UV, TOC, THM4, and HAA9 were prepared at the WWRC.

Samples were collected by UNC-CH staff during no more than a 14-hour time period twice in February and March and once in April and May of 2003. On the morning of sampling, all sample bottles were placed in several large coolers with ice packs. Upon arrival at a sample site, any faucet aerators were removed, and the faucet was turned on for five minutes if it was not running continuously. Samples were collected at outside taps when at a residence and inside faucets for businesses and treatment facilities.

Sample vials were filled at an angle while the tap was at a low flow, and filled head-space free to prevent volatilization of DBPs. Samples for temperature and free and total chlorine residuals were measured on-site. Samples for HPC, THM4, HAA9, TOC, and UV254 analyses were collected in duplicate, while a single sample was taken for temperature, free and total chlorine, ammonia, nitrite, nitrate, and AOC analyses. Samples for batch incubation studies were collected in 1 liter amber glass bottles at a point of entry into the distribution system, and stored at the temperature observed during sample collection. The batch samples were analyzed for temperature, free and total chlorine, pH, THM4, and HAA9 at 24, 48, and 72 hours after sample collection to simulate the bulk liquid phase in the distribution system. One field blank was collected at a randomly selected site for each analyte on all sample dates to analyze for contamination. The same sample collection procedure was used to obtain a sample for chloride analysis from all sample locations on two dates in February to determine the point of entry water for each sample site.

Once all of the sites had been sampled, the HPC and AOC bottles were shipped to the AWWSC laboratory in a cooler with ice packs within 24 hours of finishing sampling. The samples for inorganic nitrogen analysis were kept below 4°C overnight and delivered to Utility A's laboratory the following morning. DBPs, TOC, and UV samples were stored at 4°C in a refrigerator at the WWRC until they were analyzed, except for pH samples, which were analyzed upon returning to the laboratory.

3.5 GLASSWARE PREPARATION

The sample bottles were cleaned and prepared by the laboratory sending the bottles and analyzing the samples. AWWSC prepared the 500 mL glass AOC bottles for point of entry sampling, and the 20 mL glass bottles for HPC sampling at each site. Utility A's laboratory prepared 250 mL plastic Nalgene® bottles for nitrogen species and chloride ion analyses.

Sample glassware for DBP, TOC, and UV 254 analyses were prepared by first soaking the 40 mL bottles in tap water and detergent (Alconox Inc, New York, NY) overnight, and rinsing with laboratory grade water (LGW, Dracor Inc., Durham, NC) three times. The LGW was produced by treating tap water with a Dracor High Purity Water System (Durham, NC), which consisted of a 1.0 µm filter, 0.5 ft^3 of activated carbon, and two mixed-bed deionizers. The activated carbon removed chlorine and organic materials while the mixed-bed deionizers removed dissolved salts. After the first rinse with LGW, the glassware was immersed in a 10% nitric acid (Fisher Scientific, Fair Lawn, NJ) bath overnight, rinsed with LGW three times, rinsed with methanol (Mallinckrodt Chemicals, Phillipsburg, NJ) three times, and dried in an oven at 180°C. The 250 mL amber glass field blank bottles and 500 mL amber glass batch test bottles were prepared in the same way as the sample bottles. The plastic caps and septa for all bottles were soaked in tap water overnight, rinsed with LGW three times, rinsed with methanol three times, and left to dry in a hood for several hours. All DBP volumetric glassware was rinsed with LGW three times and with methanol once.

The THM and HAA sample bottles were prepared using preservative agents. Both THM and HAA sample bottles received approximately 20 mg of ammonium sulfate (Mallinckrodt Chemicals, Paris, KY) to quench the chlorine residual. The pH of THM sample bottles was standardized to between 4.8 and 5.5 by the addition of 0.7 g of phosphate buffer. HAA samples

were preserved using 50 μL of 80 mg/L sodium azide (Sigma-Aldrich, Milwaukee, WI) solution to discourage microbial growth.

3.6 ANALYTICAL METHODS

3.6.1 On-site Analyses

Temperature, free chlorine, and total chlorine were measured directly at the sampling sites. Temperature was initially measured with a mercury thermometer, but for the last four samplings, a Fisher Scientific Traceable® electric thermometer (Fisher Scientific, Fair Lawn, NJ) was used. Free and total chlorine were measured with a Hach® Pocket Colorimeter™ Analysis System (Hach, Loveland, CO). The Hach® sample cells were rinsed three times with the sample water and filled to the 10 mL mark with sample water. The colorimeter was zeroed using the sample water, and a pillow of N,N-diethyl-p-phenylenediamine (DPD) chlorine reagent was added to the sample cell. The sample cell was gently shaken for 20 seconds and placed in the colorimeter for analysis. The free chlorine concentration was reported to two decimal places; however, the total chlorine concentration could only be reported to one decimal place because of instrument limitations.

3.6.2 Third Party Laboratory Analyses

AOC and HPC were analyzed by AWWSC while ammonia, nitrite, nitrate, and chloride were measured by Utility A's laboratory. AOC was measured using the procedure described by LeChevallier et al (1993). HPCs were analyzed by the pour plate method in accordance with Standard Method 9215 B (1998). Samples were diluted and poured onto R2A medium within 48 hours of sample collection, and incubated for 7 days at 25°C.

Ammonia was measured as free ammonia in accordance with U.S. Environmental Protection Agency (EPA) Method 350.3 within 48 hours of sample collection (USEPA, 1979b). Nitrite and nitrate were analyzed using ion chromatography as outlined in EPA Method 300.0 (USEPA, 1993). For the sampling conducted on 2/28/03, sample analysis could not be completed within 48 hours of sample collection; therefore, sulfuric acid was added to the

samples as a preservative. The sulfuric acid addition allowed for the ammonia samples to be analyzed; however, nitrite and nitrate analyses were not possible because of the sulfuric acid addition. Chloride was analyzed using ion chromatography in accordance with EPA Method 300.0 (USEPA, 1993).

3.6.3 pH

The pH was measured for all sites with an Accumet™ Research AR10 Meter (Fisher Scientific, Fair Lawn, NJ) and an Accument™ Combination Electrode model number 13-620-531 (Fisher Scientific, Fair Lawn, NJ). The electrode was stored in pH 4 buffer (Fisher Scientific, Fair Lawn, NJ), and calibrated using a two-point calibration procedure before measuring the pH of the samples. Calibration and sample measurements were conducted while using a low speed magnetic stir-bar.

3.6.4 Ultraviolet (UV) Absorbance

UV absorbance was measured for both points of entry into the distribution system in accordance with Standard Method 5910 (Standard Methods, 1998) at 254 nm with a U-2000 UV-Visible spectrophotometer (Hitachi Instruments, Danbury, CT). Samples were removed from the refrigerator for approximately an hour to allow them to come to room temperature. A 5 cm quartz cell filled with LGW was placed into the spectrophotometer to zero the instrument. The 5 cm cell was rinsed with LGW three times and rinsed with the sample water once before being filled with the sample to take a reading. UV samples were measured in duplicate, and LGW was used to check for any instrument drift at a minimum of every ten samples. The average of the duplicate samples was checked to ensure that the percent difference was less than 10%.

3.5.6 Total Organic Carbon (TOC)

TOC was measured for both points of entry into the distribution system using Standard Method 5310B with the exception that hydrochloric acid (HCl, Fisher Scientific, Fair Lawn, NJ)

was used for acidification instead of phosphoric acid (Standard Methods, 1998). The Shimadzu 5000 Total Organic Carbon Analyzer, equipped with an ASI auto-sampler (Shimadzu Corporation, Norcross, GA), which was used to analyze the samples, is sensitive to excess phosphoric acid. TOC vials were pre-cleaned by rinsing with tap water three times, soaking the vials overnight in a 10% nitric acid bath, rinsing three times with LGW, and drying in an oven at 180°C.

Four calibration standards ranging from zero (LGW only) to 4 mg/L of TOC were prepared from dilutions of a 1000 mg/L organic carbon stock solution with LGW. The stock solution was made every three months by dissolving 2.125 g of potassium hydrogen phthalate (Fisher Scientific, Fair Lawn, NJ) into 1000 mL of LGW. Ultra-high purity air (Holox Company, Morrisville, NC) was used for the carrier gas, and LGW was used for rinsing between samples. A mechanical check of the TOC analyzer was conducted before each set of measurements while the furnace was heating.

Samples were removed from the refrigerator an hour before analysis to allow them to come to room temperature. Once at room temperature, the TOC sample vials were filled to 90% capacity and three drops of HCl were added to acidify the sample. Five drops of HCl were added to the calibration standards, and all the samples were loaded onto the auto-sampler and analyzed. A calibration standard was analyzed every ten samples, and the calibration standards were also run as unknown samples at the end of all sample analysis to ensure good quality control. Duplicate sample concentrations were averaged and checked that they did not deviate more than 10% from the average.

3.5.7 Trihalomethanes (THM4)

3.5.7.1 Analytical Procedures

The liquid-liquid extraction gas chromatographic procedure used to extract and analyze THM4 ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) samples was based on Standard Method 6232B (Standard Methods, 1998) and EPA Method 551.1 (USEPA, 1995). All THM4 analyses were conducted according to a standard operating procedure (SOP) available upon request. Samples were stored at 4°C for no more than two weeks after sample collection before the extraction was

conducted. Samples were allowed to warm to room temperature, and a 20 mL aliquot was measured using a graduated cylinder and transferred back into the sample bottle. The graduated cylinder was rinsed three times with LGW and once with sample water between each sample transfer. Four mL of methyl tert-butyl ether (MtBE, Sigma-Aldrich, Milwaukee, WI) containing 100 µg/L 1,2 dibromopropane (Sigma-Aldrich, Milwaukee, WI) was added to each sample. 1,2 dibromopropane was used as an internal standard (IS) to account for any variance in sample volume injection. Approximately 6 g of sodium sulfate (Mallinckrodt, Paris, KY) , baked at 400°C for 24 hours, was added to each sample, followed by vortex mixing (Type 16700 Mixer-MaxiMix I, Thermolyne, Dubuque, IA) for one minute. Approximately 1 mL from the middle of the MtBE layer was transferred using a Pasteur pipette to a 1.8 mL, clear glass GC auto-sampler vial (Laboratory Supply Distributors, Mt. Laurel, NJ) and capped with an aluminum PTFE-faced cap (Laboratory Supply Distributors, Mt. Laurel, NJ). The sample extracts were stored in a freezer at -15°C until analyzed by GC.

A calibration curve was prepared using two calibration standards and LGW to produce the eight calibration points listed in Table 3.1. The two calibration standards were prepared from dilutions of the individual THM species stock standards (Supelco Inc, Bellefonte, PA) in high purity methanol (Burdick & Jackson, Muskegon, MI), and stored in 5 mL amber glass bottles with open-top screw caps containing PTFE-lined silicone septa. Three matrix spikes were prepared in duplicate for each set of samples by adding two times the expected chloroform concentration with one of the calibration standards.

Table 3.1

THM species concentration for the eight calibration points.

	Concentration (µg/L)			
Level	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
1	0.00	0.00	0.00	0.00
2	1.00	0.50	0.50	0.20
3	5.00	2.50	2.50	1.00
4	10.0	5.00	5.00	2.00
5	25.0	12.5	12.5	5.00
6	50.0	25.0	25.0	10.0
7	100	50.0	50.0	20.0
8	250	125	125	50.0

Extracted samples were analyzed on a Hewlett Packard 5890A gas chromatograph (GC) with an electron capture detector (ECD, Hewlett Packard Company, Cary, NC). The operation conditions for THM4 analysis are summarized in Table 3.2. The minimum reporting level (MRL) was 1 µg/L for each THM4 species. The chromatograms for the calibration points were used to identify the retention times for the THM species and internal standard. The area under these peaks was integrated and evaluated as the ratio of the integrated area of the individual species over the integrated area for the internal standard peak, called the relative area. The concentration of the samples was determined by comparing the relative area of the sample to the relative area of the calibration standards using a calibration curve prepared from the calibration standard concentrations and relative areas.

Table 3.2

Gas chromatographic conditions for analysis of THM4.

Column	Type:	DB-1 column (Supelco, Bellefonte, PA)
	Length:	30 m
	Internal Diameter:	0.25 mm
	Film Thickness:	1.0 µm
Temperature Sequence:	Initial Temperature:	35°C, hold for 10 mins
	Ramp:	150°C at 10°C/min
	Ramp:	250°C @ 25°C/min, hold for 11 min
	Total Run Time:	36.5 min
Injector	Injector Volume:	2 µL
	Temperature:	150°C
Detector	Type:	Electron capture
	Temperature:	300°C
Gases	Carrier Gas:	Helium (Holox, Morrisville, NC)
	Carrier Flow:	1.2 mL/min @ 35°C
	Makeup Gas:	Nitrogen (Holox, Morrisville, NC)

3.5.7.2 Analytical Quality Control

Reagents and standards were run on the GC prior to extraction to verify that no contamination or degradation had occurred. New batches of MtBE and a mixture of MtBE and IS were analyzed on the GC prior to use, to confirm that the reagents were not contaminated. The THM species stock standards were discarded every six months to avoid possible degradation. Test mixes of the calibration standards were prepared from the THM standards and MtBE, and analyzed for degradation compared to the initial test mixes prepared using new THM species stock solutions. If the difference was more than 20%, the calibration standards were discarded. New calibration standards were made at least every two months.

Check standards and matrix spikes were prepared to evaluate retention time drift on the GC and recovery from the matrix, respectively. Check standards were prepared using the calibration point concentrations and analyzed at a minimum of one standard after every eight samples. A sample of MtBE and IS was injected before or after each check standard to confirm that carry over from sample to sample was not taking place. Matrix spike samples were used to check spike recoveries, with no more than ±20% variation in the calculated recovery for acceptability of the sample set.

The sample data were examined in duplicate to check for reproducibility. If the relative percent difference between duplicate samples was greater than 20%, the extraction procedure and analysis were reevaluated to identify possible sources of error. If the IS area was more than ±10% of the average IS area, the sample was removed from consideration.

The results are presented as an average of the duplicate measurements for each sample. When a duplicate sample was not available, the result of the single sample analysis is reported. If the sample and duplicate were both below the MRL, the value was reported as less than the MRL. However, if only one value was below the MRL, one half of the detection limit (0.5 µg/L for THM species) was averaged with the value above the detection limit. If the average was above the detection limit, then the average value was reported. If the average was below the MRL, the value was reported as less than the MRL.

3.5.8 Haloacetic Acids (HAA9)

3.5.8.1 Analytical Procedure

The micro liquid-liquid extraction gas chromatographic procedure used to extract and analyze HAA9 (Cl_3AA, Br_3AA, Cl_2BrAA, Br_2ClAA, Cl_2AA, Br_2AA, BrClAA, ClAA, BrAA) samples was based on Standard Method 6215B (Standard Methods, 1998) and EPA Method 552 (USEPA, 1995). All HAA analyses were conducted according to a laboratory SOP available upon request. Diazomethane was generated using two 40 mL glass vials with PFTE-lined silicone septa that were connected by 1.6 mm Teflon tubing. One of the vials was filled with 10 mL of MtBE with the Teflon tubing immersed in the MtBE (J.T. Baker, Phillipsburg, NJ), placed in an ice water bath, and a gas vent inserted into the septa. Reagent 1, consisting of 3.3 g Diazald (Sigma-Aldrich, Milwaukee, WI), 5 mL Carbitol (Sigma-Aldrich, Milwaukee, WI), and 5 mL of MtBE, was made in a 40 mL vial with PTFE-lined silicone septa and gently swirled. Reagent 2, consisting of 6 mL LGW, 10 mL high purity methanol (Burdick and Jackson, Muskegon, MI), and 4 mL potassium hydroxide (Fisher Scientific, Fair Lawn NJ), was produced in a 40 mL vial with a PTFE-lined silicone septa and gently swirled. Six mL of reagent 1 and 6 mL of reagent 2 were combined in the 40 mL vial not sitting in the ice bath, and quickly capped, with the Teflon tubing above the liquid, to capture the diazomethane gas. This gas was then trapped in the MtBE in the 40 mL vial sitting in the ice bath, turning the MtBE a vibrant yellow color. Once the MtBE had turned yellow, the 40 mL bottle was closed with a screw cap and PTFE-lined silicone septa, and placed in an explosion-proof freezer in a double-walled bomb. All glassware used for diazomethane generation was soaked in a 5 N sodium hydroxide (Mallinckrodt, Paris, KY) bath for at least 24 hours, rinsed with tap water, rinsed three times with LGW, and rinsed with methanol once.

Samples were stored at 4°C for no more than three weeks after sample collection before the extraction was conducted. Samples were allowed to warm to room temperature, and a 20 mL aliquot was measured using a graduated cylinder and transferred back into the sample bottle. The graduated cylinder was rinsed three times with LGW and once with sample water between each sample transfer. Each sample received 20 µL of 20 µg/mL 2,3 dibromopropionic acid (Supelco,

Bellefonte, PA), which served as an acid surrogate, followed by 1.5 mL of concentrated sulfuric acid (Fisher Scientific, Fair Lawn, NJ). Samples were placed in ice until they returned to room temperature, and 4 mL of MtBE with 100 µg/L of 1,2 dibromopropane (Sigma-Aldrich, Milwaukee, WI) were added. The 1,2 dibromopropane was used as an internal standard (IS), which accounted for any variance in sample volume injected into the GC. Approximately 10 g of sodium sulfate (Mallinckrodt, Paris KY), baked at 400°C for 24 hours, was added to each sample, followed by vortex mixing (Type 16700 Mixer-MaxiMix I, Thermolyne, Dubuque, IA) for one minute. Two mL of the MtBE layer were transferred by Pasteur pipette to a volumetric flask with a screw cap and PTFE-lined silicone septa. Approximately 50 mg of anhydrous, powdered magnesium sulfate (Sigma-Aldrich, Milwaukee, WI) was added to each volumetric flask to reduce the effect of water during the derivatization process (Brophy et al, 2000). The diazomethane was removed from the freezer, and 225 µL was added to each sample. The samples were refrigerated for 15 minutes and checked for yellow color, indicating that sufficient diazomethane was present to drive the esterification process. The samples were allowed to return to room temperature, and approximately 40 mg of powdered silicic acid (J.T. Baker, Phillipsburg, NJ) was added to each sample to quench any residual diazomethane. Approximately 1 mL of the derivatized sample was transferred using a Pasteur pipette to a clear glass GC auto-sampler vial (Laboratory Supply Distribution Company, Mt. Laurel, NJ) and capped with an aluminum PTFE-faced cap (Laboratory Supply Distribution Company, Mt. Laurel, NJ). The sample extracts were stored in a freezer at -15°C until analyzed by a GC.

A calibration curve was prepared using calibration standards and LGW to produce the six calibration points at 0, 2, 5, 10, 25, and 50 µg/L of each HAA9 species. The calibration standard was prepared from an HAA6 (EPA 552 Halogenated Acetic Acids Mix, Supelco Inc., Bellefonte, PA) stock standard containing 2000 µg/L of ClAA, BrAA, Cl_2AA, Br_2AA, ClBrAA, Cl_3AA, and the individual stock standards of Cl_2BrAA, $ClBr_2AA$, and Br_3AA (Supelco Inc, Bellefonte, PA) with a concentration of 1,000 µg/L each. The HAA9 standard was prepared at a concentration of 20 µg/mL for each HAA species in MtBE, and stored in an amber glass bottle and screw cap with PTFE-lined silicone septa. Three matrix spikes were prepared in duplicate for each set of samples by adding 8 to 10 mL of HAA9 standard into 25 mL of sample. Derivatized extracted samples were analyzed according to the same procedure described for THM4 in Section 3.5.7.1,

with the exception of the temperature program presented in Table 3.3. The MRL was 2 µg/L for each HAA9 species.

Table 3.3

Temperature sequence for analysis of HAA9.

Temperature Sequence:	Initial Temperature:	37°C, hold for 21 min
	Ramp:	136°C at 5°C/min, hold for 3 min
	Ramp:	250°C at 20°C/min, hold for 3 min
	Total Run Time:	52.5 min

3.5.8.2 Analytical Quality Control

The quality control strategies described in Section 3.5.7.2 for THM4 analysis were also used for HAA9 analysis including standard and sample storage; analysis of reagents, internal standard, test mixes, check standards and duplicates; and reporting of sample values, with several exceptions. The Br_3AA stock standard was replaced every 4 months and the Br_2ClAA and Cl_2BrAA stock standards were replaced every 5 months, due to increased rates of degradation of the stock standards. The HAA9 standard was produced every month due to degradation of the previously listed stock standards. In addition, if the acid surrogate concentration had a coefficient of variation greater than ±10% when compared to the average value for the entire sample set, the extraction procedure and analysis were reevaluated to identify possible sources of error.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 SELECTION OF DISTRIBUTION SYSTEM SAMPLING SITES

The characteristics of each sample location determined using the EPANET modeling software are presented in Table 4.1. Fourteen sample sites were selected with average residence times ranging from 6 to 74 hours, pipe diameters ranging from 2" to 16", and cast iron and ductile iron pipe materials. In addition, known problem areas within the distribution system were sampled, including both pressure zones. Sites 1 and 2 are point of entry locations at the two treatment plants, while the remaining sites are located throughout the distribution system.

Table 4.1

Characteristics of sample collection sites.

			Residence Time (hrs)			
Sample ID	Pipe Diameter	Pipe Material*	Max	Avg	Min	Comments
Site 1	-	-	-	-	-	Treatment Plant
Site 2	-	-	-	-	-	Treatment Plant
Site 3	12"	D	81	69	68	-
Site 4	12"	D	36	34	32	-
Site 5	4"	D	45	44	42	Dead End
Site 6	6"	C	43	41	38	Dead End
Site 7	2"	C	10	9	9	-
Site 8	4"	D	7	6	6	Dead End
Site 9	8"	D	10	8	7	-
Site 10	16"	D	6	6	5	-
Site 11	12"	D	77	64	63	High Pressure Zone
Site 12	8"	D	92	74	70	Dead End
Site 13	8"	C	12	12	11	-
Site 14	4"	D	77	74	70	High Pressure Zone

D = Ductile Iron
C = Cast Iron

Sample sites were selected to ensure flow through continually decreasing pipe diameter and the same pipe material from the point of entry into the distribution system to the point of sample collection. The sample sites listed as cast iron pipe may have received water that flowed

through sections of lined and unlined cast iron pipe as well as lined ductile iron pipe prior to the section of cast iron pipe from which the sample was taken. The water flowed through the pipe diameter listed for a minimum of one city block; however, the longest possible section of a specific pipe diameter was used in all cases.

A modified tracer study was conducted to determine the point of entry water for each sample location because the distribution system was fed by two treatment plants. The Site 1 treatment plant used ferric chloride as a coagulant at the time the tracer study was conducted, while the Site 2 treatment plant used alum. This difference in coagulants results in significantly different chloride ion concentrations leaving each treatment plant; therefore, chloride could be used as a tracer to determine the point of entry water for each sample site. Table 4.2 presents the results of the tracer study conducted on two sample dates. Site 2 appears to be the dominant point of entry water for sample Sites 3, 4, and 7, while all of the remaining sample locations receive predominantly Site 1 point of entry water. The predominant point of entry water for each sample site determined by the tracer study was assumed to remain valid for the entire four-month sample period.

Low, medium, and high categorical limits were established for the pipe diameter and residence time ranges identified for each of the sample sites. The pipe diameter stratification ranges are small (2" to 4"), medium (6" to 8"), and large (12" or greater). Residence time categories were established for low (less than 12 hours), medium (32 to 45 hours), and high (more than 64 hours) to ensure that no overlap in residence time categories occurred due to changes in water production and demand. Table 4.3 is the parameter matrix, where the sample site identification number is listed according to its characteristics.

The distribution of sample site characteristics chosen present a wide range of possible point of use attributes; in addition, the stratification of the sites provided discrete variables for comparison. Figure 4.1 is a graph of all sample site residence times, where the bar represents the average residence time and the error bars represent the maximum and minimum residence times based on EPANET model predictions. A good distribution of residence times is observed, with five, three, and four sample sites categorized as low, medium, and high residence times, respectively. Each sample site residence time is entirely defined by the categorical limits established, regardless of treated water flow and system-wide demand; therefore, the minimum and maximum residence times of any sample site do not extend into the adjacent categorical

definition. All residence time categories have one sample site receiving Site 2 point of entry water.

Table 4.2

Results of two tracer studies conducted while Site 1 used ferric chloride and Site 2 used alum as the coagulant.

	Cl^- (mg/L)	
Sample ID	2/28/2003	2/2/2003
Site 1*	26.0	-
Site 2*	11.2	-
Site 3	-	10.2
Site 4	11.6	10.3
Site 5	23.8	20.9
Site 6	27.5	25.2
Site 7	14.3	13.4
Site 8	26.6	24.9
Site 9	26.9	24.9
Site 10	25.3	25.2
Site 11	26.1	24.4
Site 12	25.8	23.8
Site 13	24.8	25.1
Site 14	26.0	25.8

* Points of Entry

Table 4.3

Parameter matrix of the stratified characteristics for each sample site.

Site 2 point of entry water is in bold; all other entries are Site 1 point of entry water.

	Water Age					
	Low ($\leq$2 hrs)		Medium (32-45 hrs)		High ($\geq$64 hrs)	
Pipe Diameter	D	C	D	C	D	C
Small (2-4")	8	**7**	5	-	14	-
Medium (6-8")	9	13	-	6	12	-
Large ($\geq$12")	10	-	**4**	-	**3**,11	-

D = Ductile Iron

C = Cast Iron

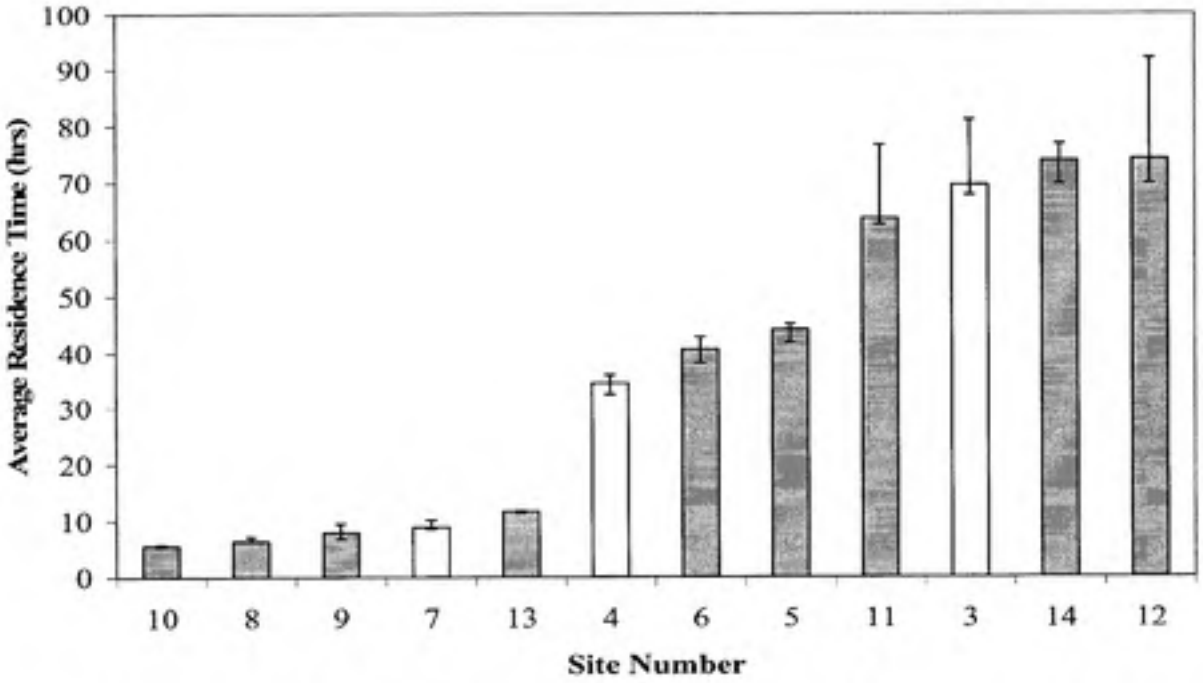

Figure 4.1 Average residence times for all sites, with maximum and minimum residence times shown by error bars. Sample sites receiving Site 1 point of entry water are in gray, and locations receiving Site 2 point of entry water are in white.

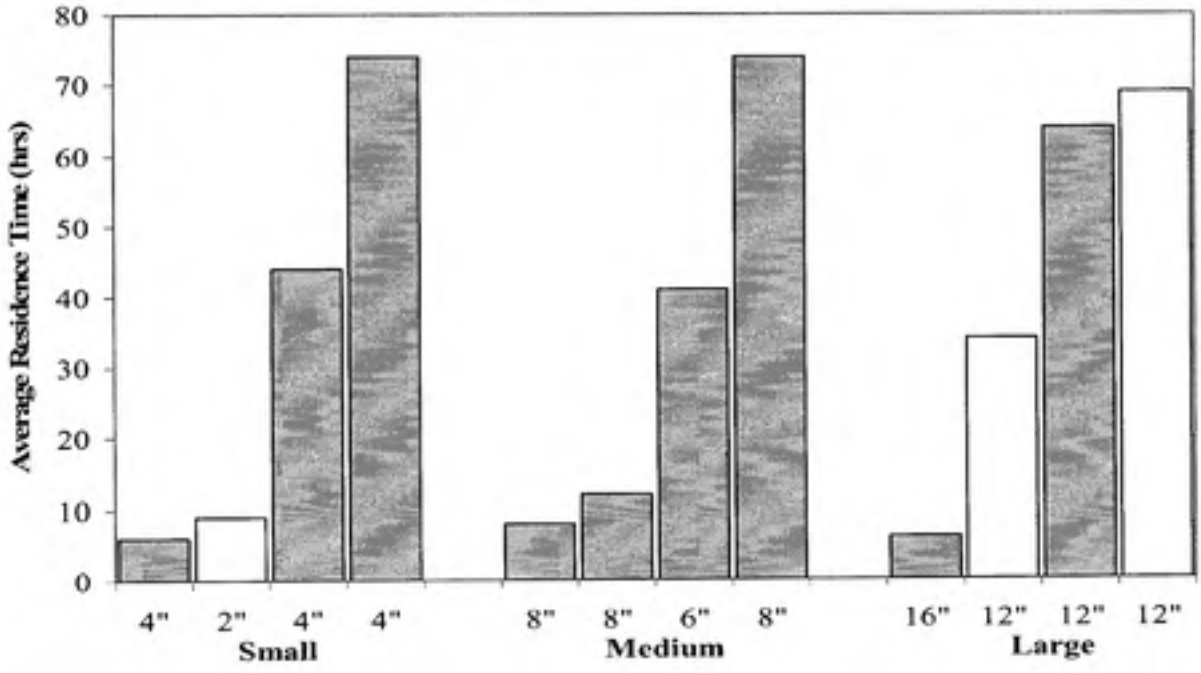

Figure 4.2 Distribution of average residence times for all pipe diameters. Locations receiving Site 2 point of entry water are in white, while sites receiving Site 1 point of entry water are gray.

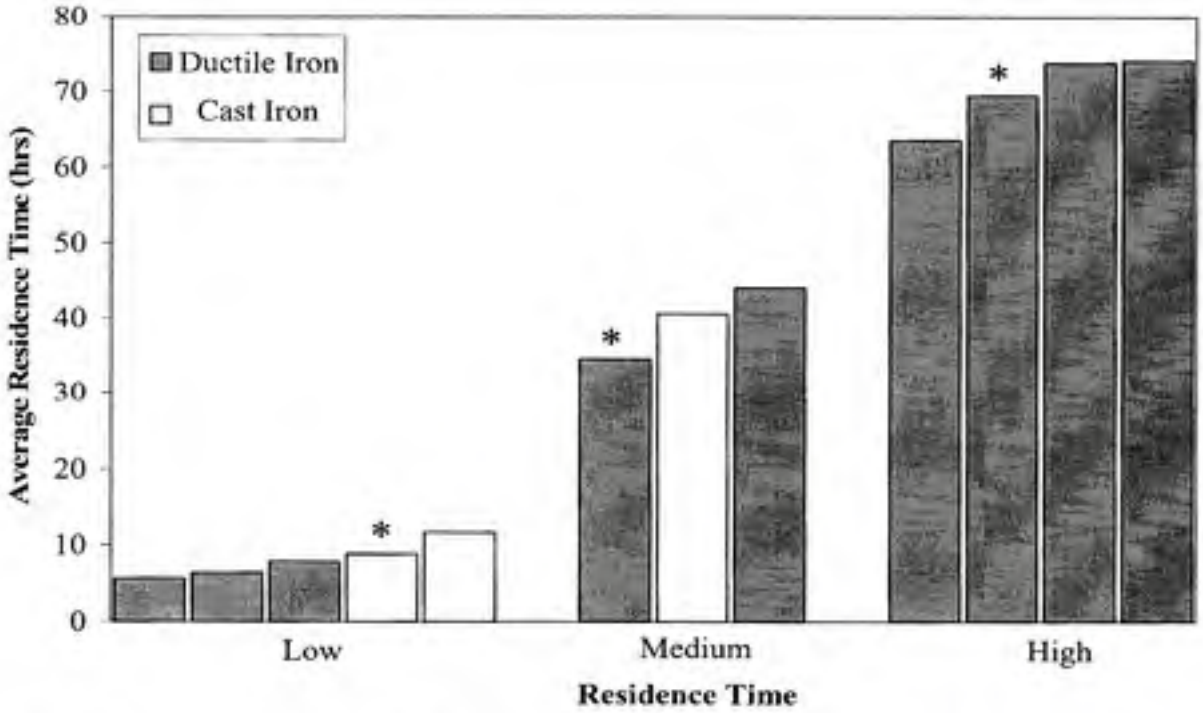

Figure 4.3 Range of average residence times for ductile iron and cast iron pipe materials. Bars with an asterisk indicate locations receiving Site 2 point of entry water.

Figure 4.2 shows the distribution of residence times for all pipe diameters organized categorically on the x-axis. Each pipe diameter category contains four sample sites, and all residence time categories are represented for each pipe diameter category. The small and large pipe diameter categories have at least one sample site receiving Site 2 point of entry water. Figure 4.3 illustrates the residence time and pipe material for each sample site organized categorically by low, medium, and high residence time. Cast iron was only present in the older, downtown area where residence times are generally low; therefore, no cast iron is present in the system for residence times greater than 48 hours.

The water treatment plant finished water flows, storage within the distribution system, and demand patterns represent possible sources of error in the estimated residence times determined from the model results. The modeled treated water flows from Site 1 at maximum, average, and low flow conditions were 21, 17, and 13.5 million gallons per day (MGD), respectively. The modeled treated water flows from Site 2 were 13, 10.5, and 9.3 MGD at maximum, average, and low flow conditions, respectively. The point of entry water flows at

Sites 1 and 2 during the four-month system-wide sampling are presented in Table 4.4. The point of entry water flows at Site 1 are within the range of water flows examined during modeling; however, the point of entry water flows from Site 2 are more than 2 MGD lower than the values used during modeling. Although the point of entry water flows at Site 2 were observed to be lower than the modeled conditions, very little change in residence time would be expected at sample sites throughout the distribution system due to decreased water production at Site 2.

Table 4.4 Water treatment plant flow rates (MGD) for all point of entry locations.

Date	Site 1	Site 2
2/11/2003	16.0	7.0
2/28/2003	17.2	6.8
3/11/2003	13.0	6.9
3/31/2003	22.5	7.0
4/29/2003	22.3	6.8
5/20/2003	19.2	7.2

The distribution system storage capacity is impacted by two storage tanks in the low pressure zone and one storage tank in the high pressure zone. An additional storage tank in the low pressure zone was under construction when this study was conducted. All of the storage tanks are operated on a fill and draw basis, and the tanks are regularly turned over to ensure that low water ages are maintained. All four of the storage tanks were included in the model used to estimate residence times at all sample locations; however, no sampling of the water entering or leaving any of the storage tanks was conducted. Therefore, the water age at many of the sample sites within the distribution system may have been affected by the age of the water being released from the storage tanks.

4.2 DISTRIBUTION SYSTEM SAMPLING

Tables 4.5 through 4.8 present illustrative example data for all chemical and biological analyses, except THMs and HAAs, for the samplings conducted on 5/20/03 during chloramination and on 3/31/03 during chlorination. Data tables for all other sample dates are presented in Appendix A.

Table 4.5

Sample site parameters and on-site data for 5/20/03, while using combined chlorine.

	Site Parameters			On-Site Data			
Sample ID	Pipe Diameter (in)	Pipe Material	Residence Time (hrs)	Temperature (°C)	pH	Free Cl_2 (mg/L)	Total Cl_2 (mg/L)
Site 1	-	-	0	17.7	8.1	0.11	2.9
Site 2	-	-	0	17.5	8.0	0.28	3.5
Site 3	12	D	74	20.2	9.2	0.14	2.6
Site 4	12	D	34	19.9	8.8	0.10	2.9
Site 5	4	D	41	21.5	9.3	0.13	3.0
Site 6	6	C	44	19.6	8.6	0.12	2.9
Site 7	2	C	9	18.5	8.2	0.13	3.5
Site 8	4	D	6	20.6	9.1	0.29	3.6
Site 9	8	D	8	17.9	8.3	0.18	3.5
Site 10	16	D	6	17.6	8.5	0.11	3.2
Site 11	12	D	69	19.1	8.6	0.14	3.3
Site 12	8	D	74	23.3	8.9	0.23	2.8
Site 13	8	C	12	17.9	8.4	0.16	3.3
Site 14	4	D	64	19.2	8.9	0.14	3.1

Table 4.6

Sample site parameters and on-site data for 3/31/03, while using free chlorine.

	Site Parameters			On-Site Data			
Sample ID	Pipe Diameter (in)	Pipe Material	Residence Time (hrs)	Temperature (°C)	pH	Free Cl_2 (mg/L)	Total Cl_2 (mg/L)
Site 1	-	-	0	13.2	6.6	3.42	3.8
Site 2	-	-	0	13.3	6.7	2.86	3.1
Site 3	12	D	74	15.1	6.8	0.74	0.9
Site 4	12	D	34	17.8	6.9	1.70	2.0
Site 5	4	D	41	15.5	7.0	1.11	1.2
Site 6	6	C	44	14.3	7.2	1.26	1.4
Site 7	2	C	9	15.7	7.1	2.78	3.2
Site 8	4	D	6	15.1	7.4	2.60	3.0
Site 9	8	D	8	13.3	7.3	3.12	3.5
Site 10	16	D	6	13.0	7.2	3.18	3.3
Site 11	12	D	69	17.2	7.2	1.50	1.7
Site 12	8	D	74	16.5	7.2	0.46	0.6
Site 13	8	C	12	13.7	7.2	3.02	3.0
Site 14	4	D	64	14.3	7.2	1.39	1.6

Table 4.7

Point of entry measurements, nitrogen species, and heterotrophic plate counts for 5/20/03, while using combined chlorine.

Sample ID	UV 254 (cm^{-1})	TOC (mg/L)	Nitrogen Species (mg/L)			HPC (cfu/mL)
			NH_3	NO_2^-	NO_3^-	
Site 1	0.037	1.57	0.43	<0.1	0.2	40
Site 2	0.043	1.82	0.18	<0.1	0.3	70
Site 3	-	-	0.23	<0.1	0.2	90
Site 4	-	-	0.22	<0.1	0.2	330
Site 5	-	-	0.17	<0.1	0.2	50
Site 6	-	-	0.20	<0.1	0.2	90
Site 7	-	-	0.13	<0.1	0.2	220
Site 8	-	-	<0.05	<0.1	0.2	25
Site 9	-	-	0.09	<0.1	0.2	60
Site 10	-	-	0.17	<0.1	0.2	20
Site 11	-	-	0.13	<0.1	0.2	60
Site 12	-	-	0.15	<0.1	0.2	160
Site 13	-	-	0.10	<0.1	0.1	<10
Site 14	-	-	0.15	<0.1	0.2	230

Table 4.8

Point of entry measurements, nitrogen species, and heterotrophic plate counts for 3/31/03, while using free chlorine.

Sample ID	UV 254 (cm^{-1})	TOC (mg/L)	AOC (µg/L)	Nitrogen Species (mg/L)			HPC (cfu/mL)
				NH_3	NO_2^-	NO_3^-	
Site 1	0.040	2.01	-	<0.05	<0.1	0.3	< 10
Site 2	0.040	2.55	347	<0.05	<0.1	0.2	<10
Site 3	-	-	-	<0.05	<0.1	0.3	130
Site 4	-	-	-	<0.05	<0.1	0.3	60
Site 5	-	-	-	<0.05	<0.1	0.3	< 10
Site 6	-	-	-	<0.05	<0.1	0.3	< 10
Site 7	-	-	-	<0.05	<0.1	0.3	< 10
Site 8	-	-	-	<0.05	<0.1	0.3	< 10
Site 9	-	-	-	<0.05	<0.1	0.3	< 10
Site 10	-	-	-	<0.05	<0.1	0.3	< 10
Site 11	-	-	-	<0.05	<0.1	0.3	20
Site 12	-	-	-	<0.05	<0.1	0.3	170
Site 13	-	-	-	<0.05	<0.1	0.3	< 10
Site 14	-	-	-	<0.05	<0.1	0.3	5

At both points of entry into the distribution system, samples were taken for total organic carbon (TOC), ultraviolet absorbance (UV 254), and assimilable organic carbon (AOC) analyses.

The treated water TOC concentrations were moderate, ranging from 1.5 to 2.2 mg/L for Site 1 and 1.8 to 2.6 mg/L for Site 2 during the sampling period. The UV 254 absorbance readings were between 0.026 and 0.046 cm^{-1} for Site 1 and 0.031 and 0.050 cm^{-1} for Site 2. The organic concentrations were higher for Site 2 than Site 1 based on the analyses conducted during this study, which is consistent with historical organic carbon measurements. The concentration of AOC at both plants ranged from less than 200 µg/L to more than 500 µg/L over the study period. The AOC concentrations for both water treatment plants were highly variable from one sample date to the next, which is consistent with historical data for Utility A.

Temperature and pH were measured throughout the distribution system for all sample dates. The temperature ranged from 6 to 24°C during the study period. Higher temperatures were observed for the samplings conducted in April and May compared to the February and March temperatures. The pH differed significantly with the secondary disinfectant used. During chloramination, the pH was generally above 8 but not greater than 9. The pH for the April sampling was slightly lower than the other sample dates conducted during chloramination. The pH was lower when free chlorine was used as a secondary disinfectant, ranging from 6.5 to 7.7 through the distribution system.

4.2.1 Comparison of Disinfectant Residuals

Free chlorine and combined chlorine were used as disinfectants during the course of this study, and each disinfectant exhibited unique characteristics within the distribution system. The total chlorine concentrations at the points of entry into the distribution system averaged 3.5 mg/L during the four samplings conducted during chloramination (A total chlorine concentration of 4.7 mg/L was observed for Site 2 on 2/28/03; however, this value is probably incorrect based on the normal combined chlorine concentrations seen throughout the rest of the study.). The total chlorine concentration decreased through the distribution system to a minimum of 2.6 mg/L during chloramination (see Table 4.5 and Appendix A). As was expected, significant free chlorine residuals were not observed while using combined chlorine as the secondary disinfectant. Increases in temperature did not correlate to decreased total chlorine residuals for the samples collected in this study.

For disinfection with free chlorine, the majority of the chlorine residual was measured as free chlorine. Free chlorine concentrations ranged from 2.7 to 3.4 mg/L at the point of entry from both treatment plants on the two sampling dates conducted during chlorination. For the first sampling date (3/11/03), the free chlorine residual decreased to zero at two of the sample sites with high residence times (see Appendix A); however, both water treatment plants were in the process of increasing chlorine feed concentrations in an attempt to maintain a residual at all points within the distribution system. Therefore, the chlorine concentrations fed at the water treatment plants on the day of sampling were higher than the corresponding chlorine feed concentrations associated with the water sampled at sites with high residence times due to the lag time between the points of entry and the sites with high residence times. By the time of the second sampling conducted while using free chlorine as a secondary disinfectant, all points within the distribution system had a residual free chlorine concentration of at least 0.5 mg/L. The free chlorine residual decreased with increasing residence time through the distribution system during chlorination (See Table 4.6 and Appendix A).

Figure 4.4 shows the average total chlorine concentration during chloramination and the average free chlorine concentration during chlorination for the estimated residence time of each sample site, with the error bars representing the maximum and minimum chlorine concentrations. The combined chlorine concentration remained relatively stable throughout the distribution system; however, the free chlorine concentration tended to decrease with increasing residence time. These trends were expected because combined chlorine is a relatively weak oxidant, whereas free chlorine is readily reduced by organic and inorganic material. Similar behavior was observed for Site 1 and Site 2 point of entry water.

Pipe diameter and pipe material did not have an effect on the decay of free chlorine in the distribution system. Figure 4.5 shows the free chlorine concentration as residence time increases for small, medium, and large diameter pipes on 3/31/03. Although a clear trend of decreasing free chlorine concentration with increasing residence time is observed, small pipe diameters did not exert an increased chlorine demand when compared to large diameter pipes. Other researchers found that pipe diameter effects were only significant in diameters less than 3" at residence times less than 9 hours (Lu et al, 1999; Kienen et al, 1999); therefore, no trend was expected between pipe diameter and free chlorine concentration in this study.

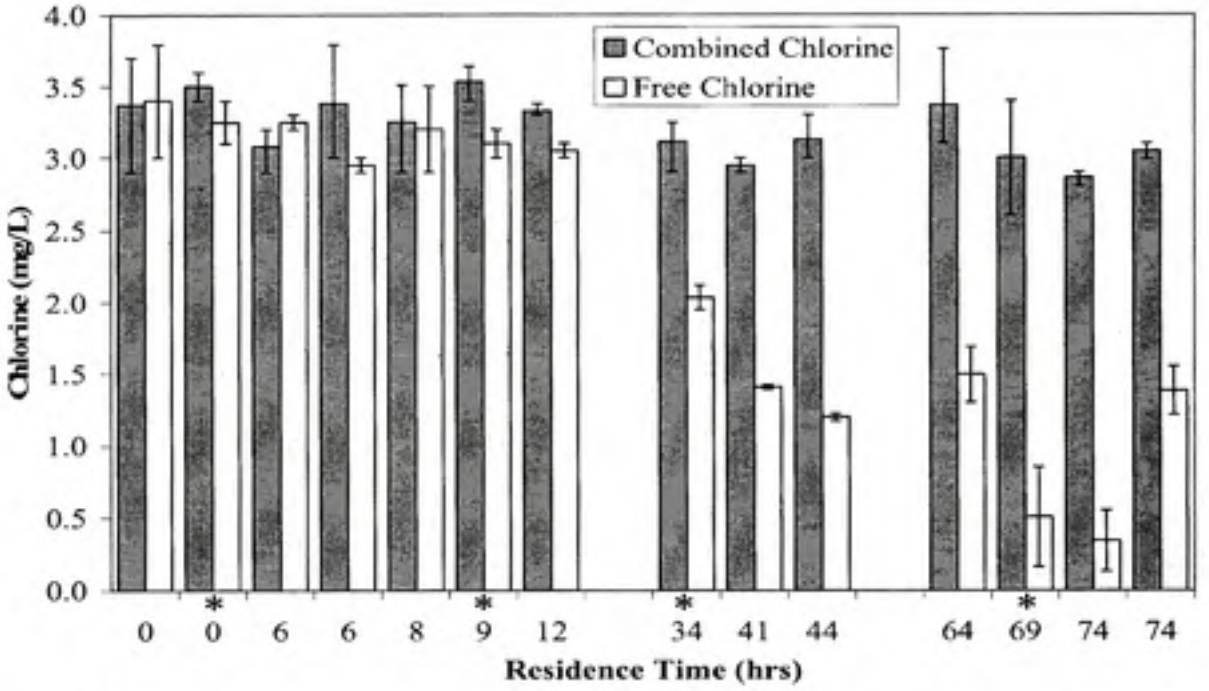

Figure 4.4 Comparison of average residual chlorine concentrations for all residence times when free chlorine and combined chlorine were used as disinfectants. An asterisk indicates Site 2 point of entry water.

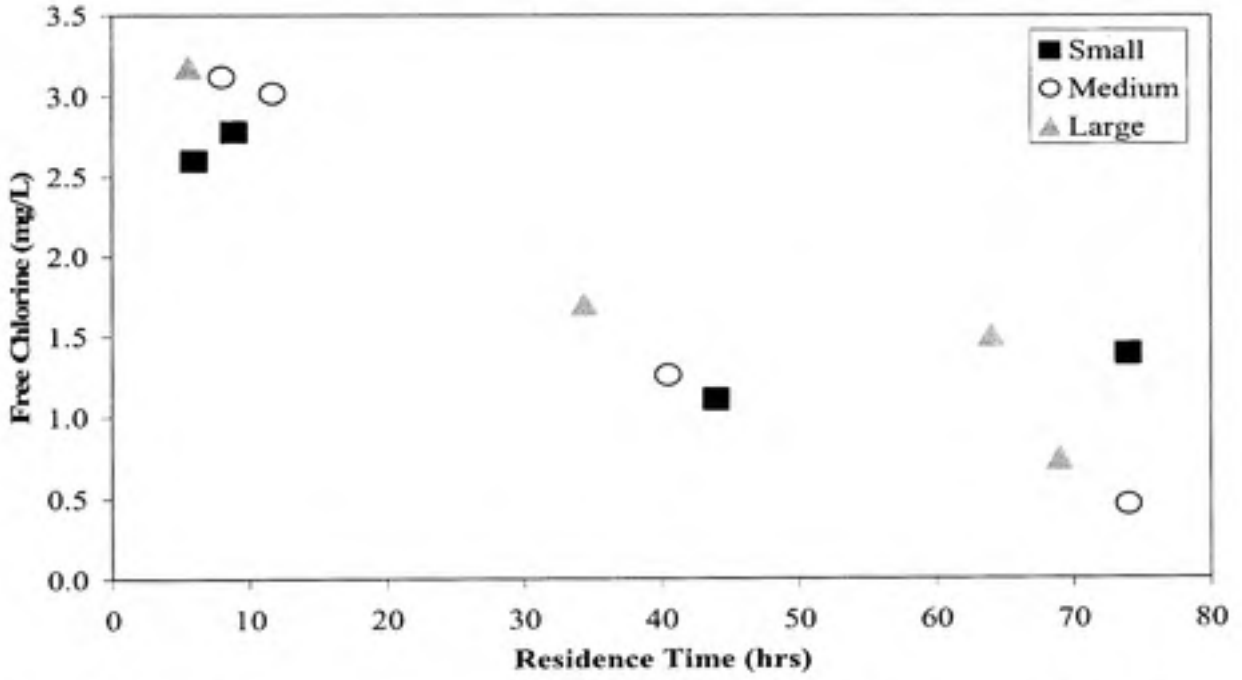

Figure 4.5 Free chlorine concentrations in small, medium, and large diameter pipes over the range of residence times on 3/31/03.

Figure 4.6 shows the free chlorine concentration for low and medium residence time sample sites with either cast iron or ductile iron pipes on 3/31/03. Differences in pipe material did not result in differences in the rate of chlorine decay. Similar results were obtained for the sampling conducted on 3/11/03. Figures comparing pipe diameter and pipe material and chlorine decay on 3/11/03 are presented in Appendix B.

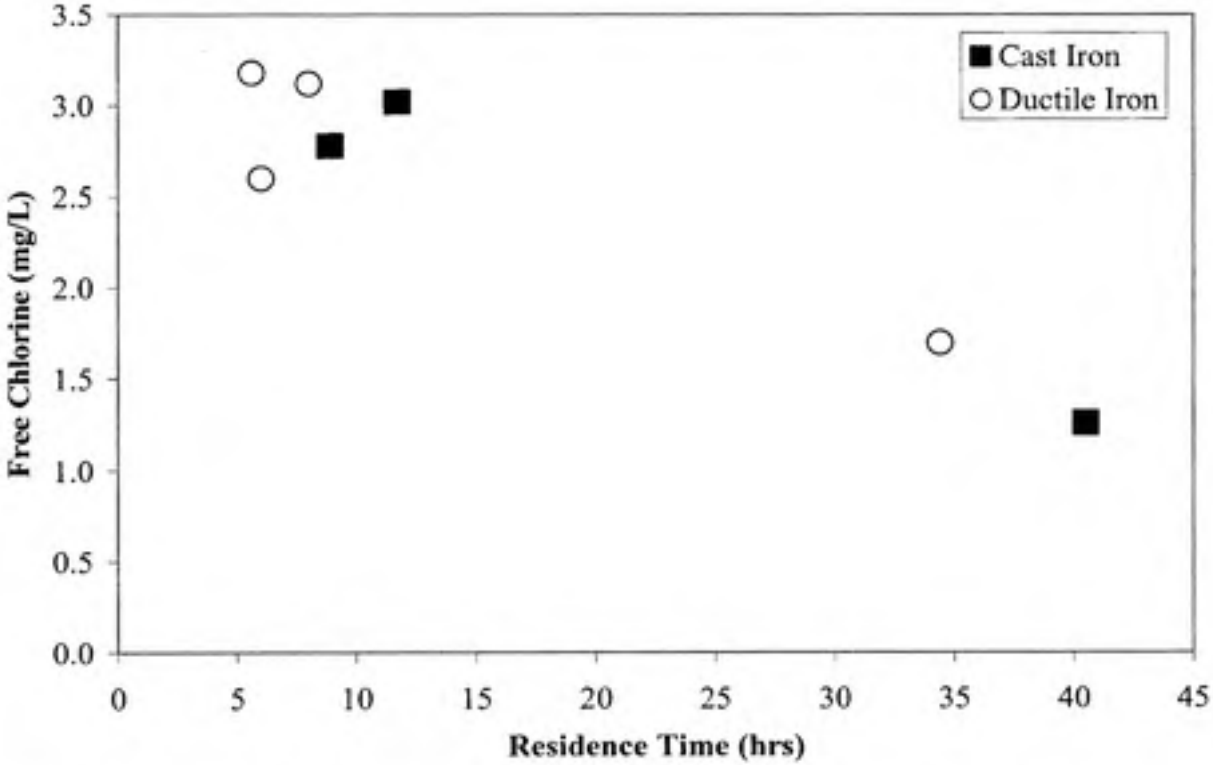

Figure 4.6 Free chlorine concentrations in cast iron and ductile iron pipes for low and medium residence times on 3/31/03.

4.2.1.1 Effect on HPCs

The type of secondary disinfectant used did not significantly affect HPCs during this study. However, based on historical data for Utility A's distribution system, combined chlorine disinfection results in lower HPCs than free chlorine disinfection (DiGiano, 2003). Figure 4.7 presents the HPCs over all residence times for all sampling dates, except 2/28/03 when analysis could not be conducted because of sample holding time constraints. The HPCs did not differ

significantly during the free chlorine disinfection period when compared to the combined chlorine disinfection period. Elevated HPCs were observed even when the combined chlorine concentration was above 3 mg/L and the free chlorine concentration was approximately 2 mg/L. This is consistent with historical data for this distribution system, where HPCs as high as 1000 cfu/mL have been observed in the presence of a 3 mg/L free chlorine residual during chlorination (DiGiano, 2003). The highest HPC observed in this study was 675 cfu/mL at Site 3 on 5/20/03, which occurred in the presence of a 2.9 mg/L combined chlorine residual. This high concentration is still almost two orders of magnitude lower than the maximum HPC observed during a previous study when the secondary disinfectant was free chlorine (DiGiano, 2003).

In Figure 4.7, the last two sample dates, April and May, tend to have higher HPCs throughout the entire distribution system than the other sample dates. This increase in HPC concentration is probably the result of increasing temperatures. Increased biological activity within the distribution system during warm temperatures is consistent with the observations of other researchers (Colbourne et al, 1991; LeChevallier et al, 1996; Prevost et al, 1998; Lu et al, 1999; Baribeau et al, 2000; DiGiano et al, 2001).

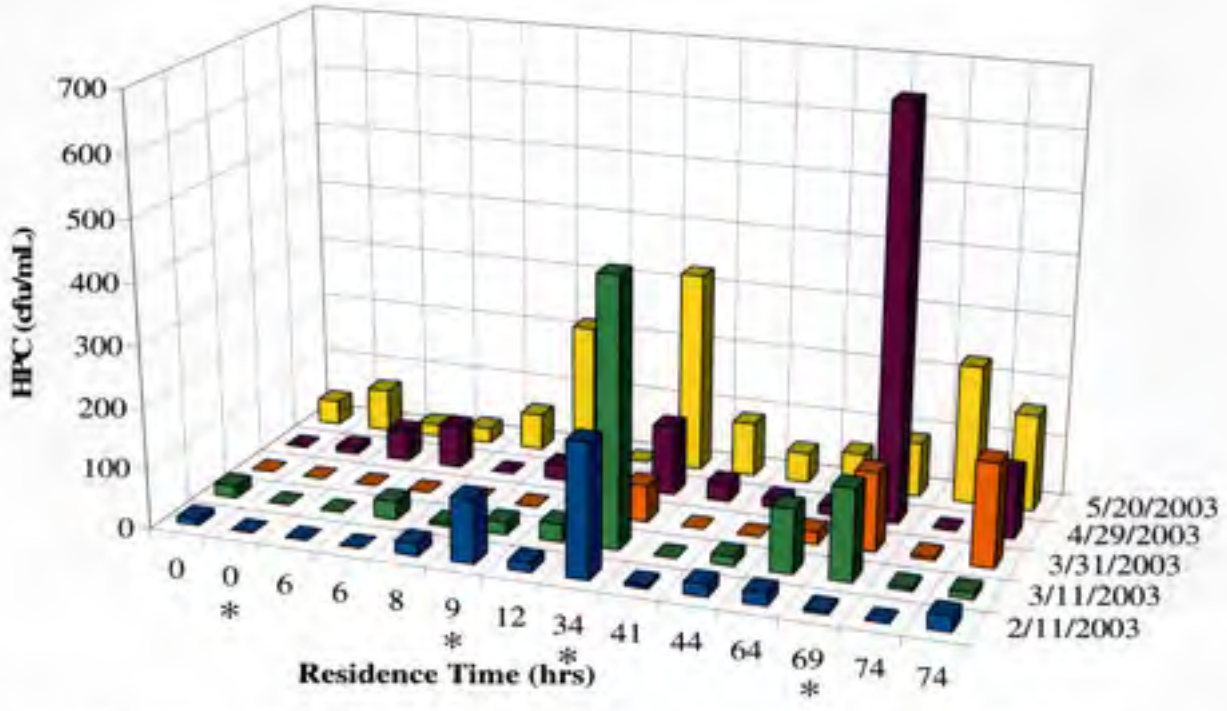

Figure 4.7 HPCs over the range of residence times for all sample dates except 2/28/03. An asterisk indicates Site 2 point of entry water.

The point of entry water for each sample site had a significant effect on HPCs, as shown in Figure 4.8. Sample sites using Site 2 point of entry water had higher HPCs when compared to sample sites receiving Site 1 point of entry water. In general, HPCs increased with increasing residence time for both treated water sources.

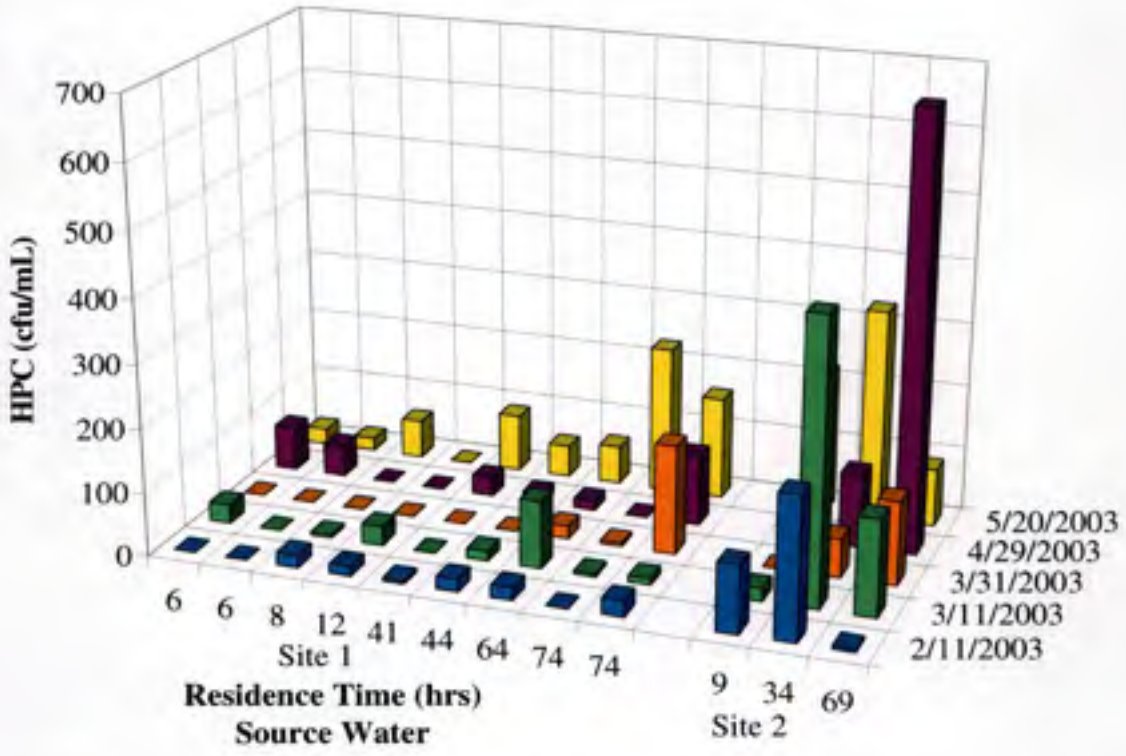

Figure 4.8 HPCs ordered by source water for all residence times and sample dates except 2/28/03.

Pipe diameter and pipe material did not appear to have a significant impact on the HPCs observed within the distribution system. Figure 4.9 shows the HPCs for all residence times and sample dates (except 2/28/03) categorized by pipe diameter. The large diameter pipes appear to have higher HPCs than the small diameter pipes. However, the large pipe diameter category has two sample sites that received Site 2 point of entry water and two sample sites that had water with long residence times. Therefore, the large pipe diameter stratum is more heavily weighted with additional factors that may contribute to high HPCs when compared to the other pipe diameter categories.

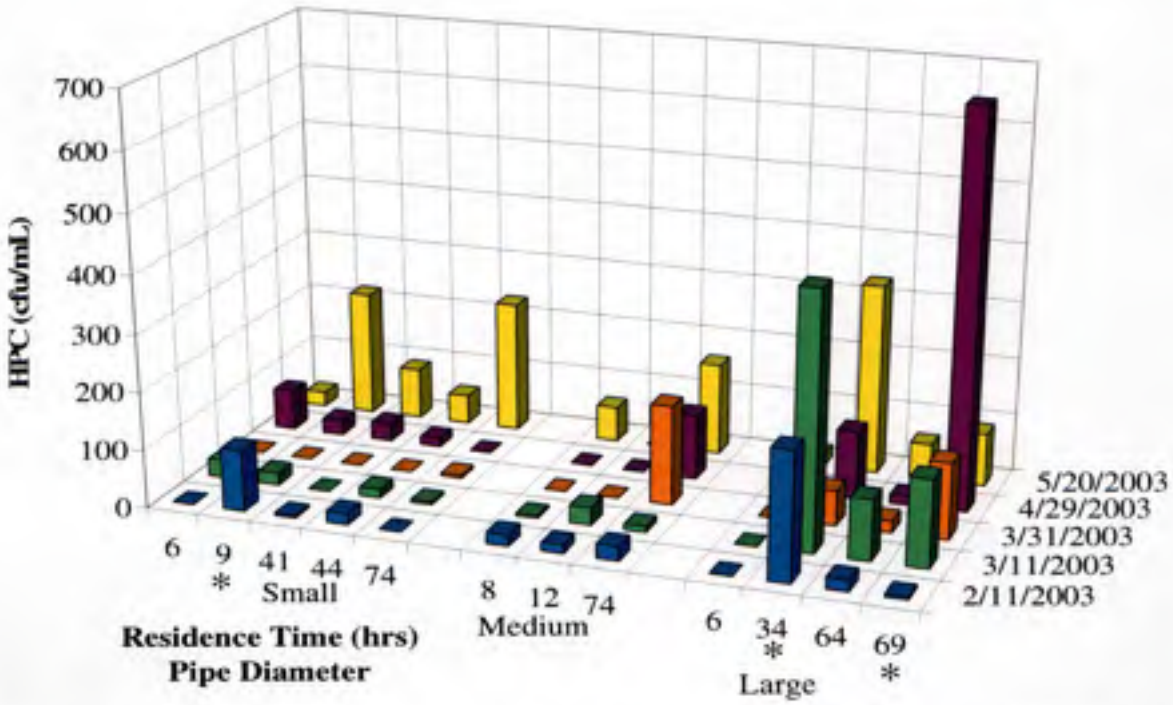

Figure 4.9 HPCs for different pipe diameter categories on all sample dates except 2/28/03. An asterisk indicates Site 2 point of entry water.

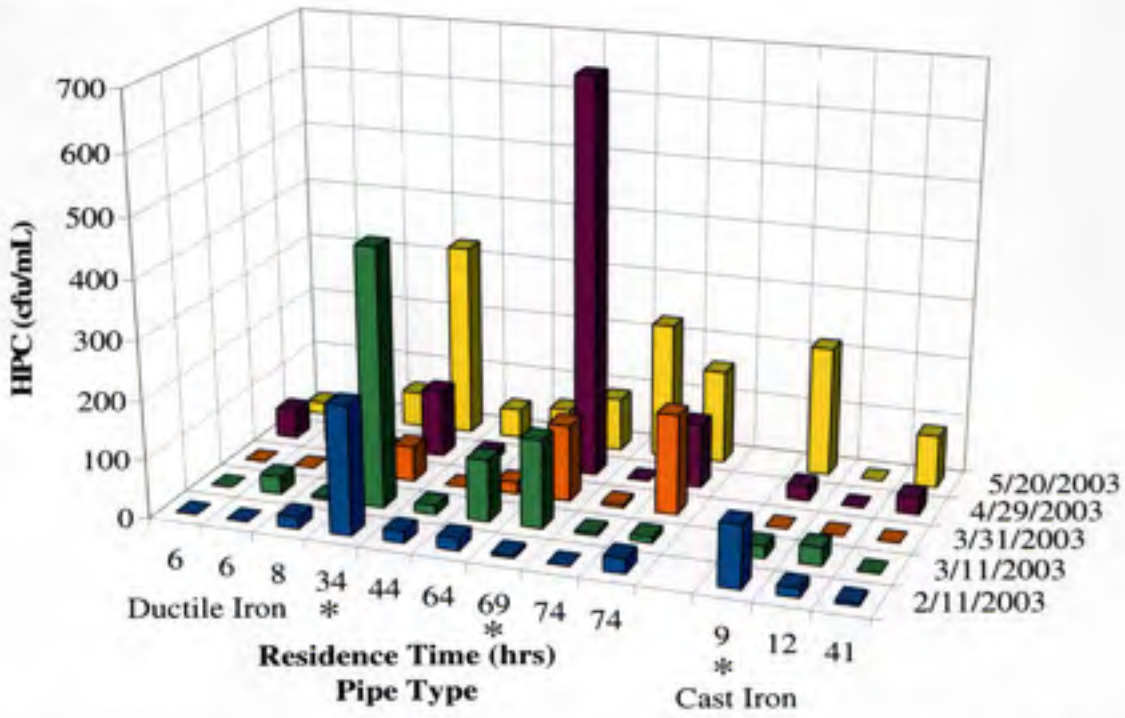

Figure 4.10 HPCs for cast iron and ductile iron pipe materials on all sample dates except 2/28/03. An asterisk indicates Site 2 point of entry water.

Figure 4.10 presents the HPCs for all residence times and sample dates (except 2/28/03) categorized by pipe material. Although the ductile iron material appears to have higher HPCs than cast iron, these results are misleading because the ductile iron category is more heavily weighted with Site 2 point of entry water and high residence time sample sites.

4.2.1.1 Effect on Nitrogen Species Concentrations

The ammonia, nitrite, and nitrate concentrations did not change significantly through the distribution system when combined chlorine was used as a secondary disinfectant. Figure 4.11 presents the ammonia concentration for all residence times and sample dates during chloramination, with Site 2 point of entry water indicated by an asterisk. An abnormally high free ammonia concentration was observed for both water treatment plants on 2/28/03; however, the remaining combined chlorine sample dates had free ammonia concentrations near or below 0.4 mg/L as nitrogen. The nitrite concentration was consistently below the detection limit (0.1 mg/L) throughout the distribution system on all sample dates, and the nitrate concentration was between 0.2 and 0.4 mg/L (see Table 4.7 and Appendix A). Nitrite and nitrate were not analyzed on 2/28/03 due to sample holding time constraints.

No evidence of nitrification was observed during this study. Although the ammonia concentration decreased slightly on several occasions, these decreases did not correspond to increased nitrite or nitrate concentrations. In addition, combined chlorine concentrations above 2.5 mg/L were maintained throughout the distribution, which should have limited the growth of ammonia-oxidizing and nitrite-oxidizing bacteria.

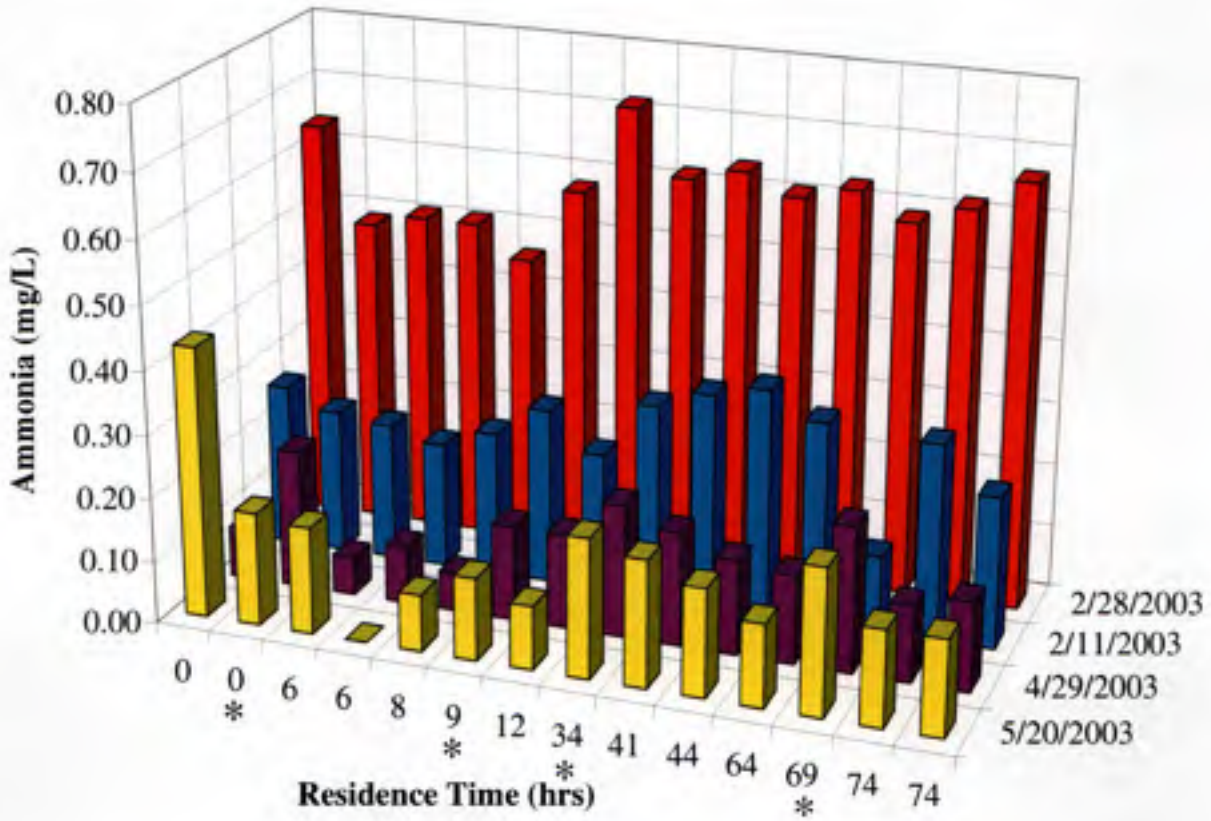

Figure 4.11 Ammonia concentrations over the range of residence times for all sample dates during chloramination. An asterisk indicates Site 2 point of entry water.

4.2.2 Disinfection By-Product Formation

Tables 4.9 through 4.12 present illustrative, example THM and HAA data for the samplings conducted on 5/20/03 during chloramination and on 3/31/03 during chlorination. Data tables for all other sample dates are presented in Appendix A. Table 4.13 is a summary of the THM4 concentrations for all sample sites on all sampling dates, with Site 2 point of entry water sample sites in bold. Table 4.14 is a corresponding summary of the HAA9 concentrations for all sample sites on all sample dates.

Table 4.9

Trihalomethane concentrations (µg/L) for 5/20/03, while using combined chlorine.

Sample ID	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	THM4
Site 1	42.8	5.6	<1	<1	48.3
Site 2	57.5	6.0	<1	<1	63.5
Site 3	70.2	5.7	<1	<1	75.9
Site 4	61.4	5.7	<1	<1	67.1
Site 5	67.7	5.8	<1	<1	73.4
Site 6	63.2	5.9	<1	<1	69.1
Site 7	60.7	6.1	<1	<1	66.8
Site 8	62.7	6.6	<1	<1	69.3
Site 9	56.1	6.6	<1	<1	62.7
Site 10	53.8	6.5	<1	<1	60.3
Site 11	62.3	5.8	<1	<1	68.1
Site 12	68.1	5.9	<1	<1	74.0
Site 13	53.8	5.8	<1	<1	59.6
Site 14	63.7	5.7	<1	<1	69.4

Table 4.10

Trihalomethane concentrations (µg/L) for 3/31/03, while using free chlorine.

Sample ID	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	THM4
Site 1	55.8	5.5	<1	<1	61.3
Site 2	68.6	5.8	<1	<1	74.4
Site 3	162	12.6	<1	<1	175
Site 4	110	9.6	<1	<1	120
Site 5	136	12.4	<1	<1	149
Site 6	109	12.1	<1	<1	121
Site 7	76.2	7.3	<1	<1	83.5
Site 8	85.0	8.8	<1	<1	93.8
Site 9	66.9	7.0	<1	<1	73.9
Site 10	60.6	6.7	<1	<1	67.3
Site 11	104	11.6	<1	<1	116
Site 12	124	13.7	<1	<1	138
Site 13	68.7	8.2	<1	<1	76.9
Site 14	103	12.9	<1	<1	117

Table 4.11

Haloacetic acid concentrations (µg/L) for 5/20/03, while using combined chlorine.

Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
Site 1	7.4	<2	24.0	<2	26.9	<2	4.7	<2	<2	63.0
Site 2	6.1	<2	25.8	<2	25.8	<2	4.5	<2	<2	62.2
Site 3	7.0	<2	31.8	<2	26.8	<2	3.6	<2	<2	69.2
Site 4	7.0	<2	25.7	<2	23.8	<2	4.2	<2	<2	60.6
Site 5	5.3	<2	29.7	<2	27.4	<2	4.2	<2	<2	66.6
Site 6	4.5	<2	27.7	<2	28.8	<2	4.6	<2	<2	65.5
Site 7	4.6	<2	24.8	<2	26.6	<2	4.5	<2	<2	60.4
Site 8	5.9	<2	25.1	<2	27.1	<2	5.1	<2	<2	63.1
Site 9	8.0	<2	24.8	<2	28.1	<2	4.6	<2	<2	65.6
Site 10	6.1	<2	24.4	<2	27.6	<2	5.0	<2	<2	63.2
Site 11	8.9	<2	27.5	<2	27.5	<2	4.7	<2	<2	68.7
Site 12	5.5	<2	37.6	<2	25.7	<2	4.0	<2	<2	72.9
Site 13	8.4	<2	23.3	<2	26.6	<2	4.8	<2	<2	63.0
Site 14	4.9	<2	26.4	<2	27.3	<2	4.4	<2	<2	63.0

Table 4.12

Haloacetic acid concentrations (µg/L) for 3/31/03, while using free chlorine.

Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
Site 1	<2	<2	36.8	2.2	41.0	<2	5.1	<2	<2	85.2
Site 2	2.3	<2	39.9	<2	48.1	<2	4.6	<2	<2	94.8
Site 3	6.0	<2	61.0	3.0	71.1	<2	3.9	<2	<2	145
Site 4	4.6	<2	49.9	2.4	68.1	<2	3.8	<2	<2	129
Site 5	6.7	<2	60.1	3.3	64.3	<2	6.5	<2	<2	141
Site 6	5.1	<2	50.7	3.2	60.3	<2	7.0	<2	<2	126
Site 7	3.8	<2	41.4	2.8	56.5	<2	5.6	<2	<2	110
Site 8	4.4	<2	43.1	2.7	53.0	<2	6.3	<2	<2	109
Site 9	3.6	<2	41.3	2.5	53.0	<2	6.7	<2	<2	107
Site 10	5.4	<2	39.6	2.4	50.1	<2	3.7	<2	<2	101
Site 11	6.4	<2	52.5	3.8	65.3	<2	7.4	<2	<2	135
Site 12	6.1	<2	55.4	3.4	66.5	<2	5.4	<2	<2	137
Site 13	3.4	<2	41.5	2.6	54.7	<2	7.2	<2	<2	109
Site 14	3.9	<2	53.7	3.3	61.4	<2	6.9	<2	<2	129

Table 4.13

Summary of THM4 (µg/L) data for all sample dates. Site 2 point of entry water is noted in bold and an asterisk indicates free chlorine as the secondary disinfectant.

Sample ID	2/11/2003	2/28/2003	3/11/2003*	3/31/2003*	4/29/2003	5/20/2003
Site 1	37.1	42.5	38.3	61.3	54.8	48.3
Site 2	**46.8**	**53.8**	**50.2**	**74.4**	**63.5**	**63.5**
Site 3	**70.3**	**66.4**	**131**	**175**	**86.5**	**75.9**
Site 4	**61.3**	**62.4**	**91.6**	**120**	**82.0**	**67.1**
Site 5	63.3	60.1	94.1	149	78.5	73.4
Site 6	59.1	59.7	81.6	121	76.7	69.1
Site 7	**53.1**	**52.1**	**54.3**	**83.5**	**71.1**	**66.8**
Site 8	49.4	46.5	52.2	93.8	72.3	69.3
Site 9	52.8	46.6	55.0	73.9	66.1	62.7
Site 10	46.8	47.5	47.3	67.3	64.4	60.3
Site 11	57.8	57.0	79.6	116	77.3	68.1
Site 12	63.1	60.8	98.7	138	80.4	74.0
Site 13	50.9	50.1	55.8	76.9	69.5	59.6
Site 14	58.5	55.4	79.1	117	80.6	69.4

Table 4.14

Summary of HAA9 (µg/L) data for all sample dates. Site 2 point of entry water is noted in bold and an asterisk indicates free chlorine as the secondary disinfectant.

Sample ID	2/11/2003	2/28/2003	3/11/2003*	3/31/2003*	4/29/2003	5/20/2003
Site 1	59.4	57.7	61.5	85.2	64.9	63.0
Site 2	**57.5**	**56.0**	**72.4**	**94.8**	**61.3**	**62.2**
Site 3	**65.7**	**58.1**	**96.2**	**145**	**82.3**	**69.2**
Site 4	**54.7**	**59.0**	**104**	**129**	**74.8**	**60.6**
Site 5	58.0	59.1	90.5	141	73.8	66.6
Site 6	56.7	61.4	88.6	126	69.5	65.5
Site 7	**58.7**	**57.1**	**81.1**	**110**	**65.4**	**60.4**
Site 8	56.9	52.8	78.3	109	70.6	63.1
Site 9	58.8	54.6	79.6	107	67.9	65.6
Site 10	50.9	57.9	71.8	101	68.0	63.2
Site 11	56.6	58.6	91.1	135	73.9	68.7
Site 12	64.1	63.5	88.0	137	75.7	72.9
Site 13	55.1	58.0	80.0	109	69.6	63.0
Site 14	59.4	58.4	92.1	129	72.0	63.0

Chloroform was the predominant THM4 species, ranging from 83% to 93% of the total THM concentration over the course of the study. Bromodichloromethane constituted the remaining portion of the THM4 concentration. The high proportion of chloroform was expected based on the low bromide concentration in Utility A's raw water source. The speciation of THM4 was not affected by temperature or disinfectant type, concentration, and contact time.

The trihaloacetic acids (X_3AA) were slightly more dominant than the dihaloacetic acids (X_2AA) for both disinfectants used in the distribution system. Table 4.15 presents the maximum, average, and minimum percent of each class of HAA9 species, on a molar basis. Dichloroacetic acid (Cl_2AA) and trichloroacetic acid (Cl_3AA) were the predominant HAA species formed, and were approximately equal in concentration while using combined chlorine for disinfection. A slightly higher concentration of Cl_3AA was produced while using free chlorine for disinfection compared to Cl_2AA. In addition, small concentrations of chloroacetic acid (ClAA), bromochloroacetic acid (BrClAA), and bromodichloroacetic acid ($BrCl_2AA$) were produced. As mentioned previously, the raw water source for both treatment plants contains very little bromide; therefore, low concentrations of bromine-containing DBPs were expected. The speciation of HAA9 was not affected by temperature or disinfectant concentration and contact time. Other researchers have observed higher concentrations of X_3AA than X_2AA during chlorination; however, X_2AA concentrations usually exceed X_3AA concentrations when combined chlorine is used as a disinfectant (Cowman and Singer, 1996; Symons et al, 1998; Zhang et al, 2000). The high percentage of X_3AA observed during chloramination may be due in part to the use of free chlorine as the primary disinfectant throughout the study period.

Table 4.15 Molar distribution of HAA9 classes.

	XAA	X_2AA	X_3AA
Maximum	19%	52%	57%
Average	9%	42%	49%
Minimum	0%	36%	41%

4.2.2.1 Trihalomethanes (THM4)

Figure 4.12 presents the average THM4 concentrations as residence time increases for sampling conducted while using combined chlorine or free chlorine for secondary disinfection. The error bars represent the maximum and minimum THM4 concentrations. The THM4 concentrations increased with increasing residence time when free chlorine was the secondary disinfectant; whereas, the THM4 concentrations remained relatively uniform during chloramination. Appreciable increases in THM4 concentrations within the distribution system during chlorination were expected based on work conducted by other researchers (Zhang et al, 2000; Baribeau et al, 2000; Singer, 2001). Similarly, chloramination is known to arrest THM formation (Wolfe et al, 1984; Johnson and Jensen, 1986; Stevens et al, 1989; Cowman and Singer, 1996; Symons et al, 1998; Zhang et al, 2000; Baribeau et al, 2000).

Figure 4.13 shows the THM4 concentrations for all residence times and all six sample dates categorized by point of entry water. The point of entry water did not have any discernable effect on the THM4 concentration observed in the distribution system. The THM4 concentration is higher for the last two sample dates (4/29/03, 5/20/03) than for the first two sample dates (2/11/03, 2/28/03). This difference is probably the result of increased temperatures during the last two sample dates (13 to 24°C) when compared to the first two dates (6 to 12°C). Increased formation of THM4 within the treatment plant is expected at higher temperatures due to the increased rate of reaction between free chlorine and organic material (Peters et al, 1980; Krasner et al, 1989; Singer, 1994; Hooper and Owen, 1994; Singer et al, 1995; Krasner et al, 1996; Arora et al, 1997; Lebel et al, 1997; Chen and Weisel, 1998; Baribeau et al, 2000; Singer, 2001).

The THM4 concentrations are lower for the first set of samples taken during chlorination (3/11/03) than for the second set of samples (3/31/03) because Utility A was still in the process of adjusting chlorine feed concentrations on 3/11/03 to maintain a free chlorine residual throughout the distribution system. Therefore, the waters that were sampled at the high residence time sites on 3/11/03 had been treated with a lower chlorine dose than the waters that were sampled at low residence time sites. The increased chlorine feed concentration over time resulted in increased THM4 concentrations throughout the distribution system. Many other researchers have also observed increased DBP formation when higher disinfectant doses were applied (Singer, 1994; Hooper and Owen, 1994; Stevens et al, 1989; Elshorbagy, 2000; Singer, 2001).

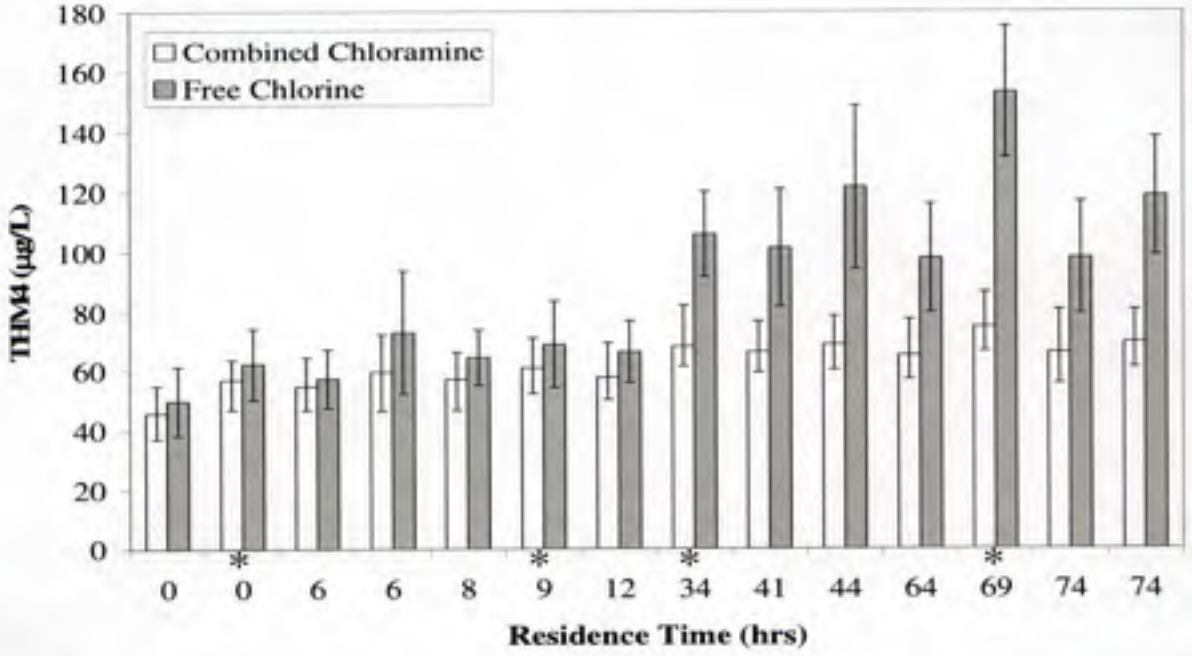

Figure 4.12 Average concentrations of THM4 for samplings conducted while using combined chlorine or free chlorine for disinfection over the range of residence times. An asterisk indicates Site 2 point of entry water.

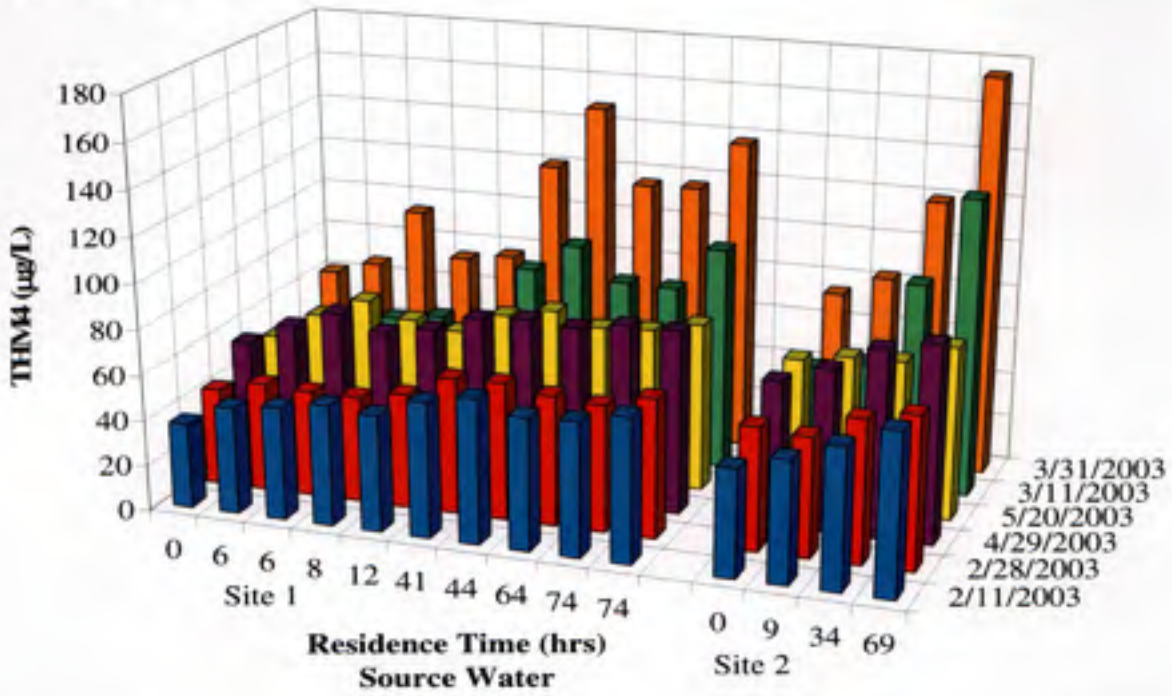

Figure 4.13 Concentrations of THM4 over the range of residence times for all sample dates, organized by point of entry water.

Although, the regulatory MCL for THM4 of 80 µg/L is based on an annual average of four quarterly samples collected from the distribution system for each treatment plant, the concentration exceeded the regulatory limit at three sample sites on 4/29/03 when combined chlorine was used as the secondary disinfectant. In contrast, the THM4 concentration was above the 80 µg/L MCL at essentially all of the sample sites for both free chlorine sample dates (3/11/03, 3/31/03). The maximum THM4 concentration of 175 µg/L during chlorination was more than twice the regulatory limit. Secondary disinfection with combined chlorine is considered to be an effective technology to reduce THM4 formation in the distribution system and help meet current and future regulatory limits.

4.2.2.2 Haloacetic Acids (HAA9)

Figure 4.14 presents the average HAA9 concentrations as residence time increases for sampling conducted while combined chlorine or free chlorine were used for secondary disinfection. The error bars represent the maximum and minimum HAA9 concentrations. The HAA9 concentration increased with increasing residence time during chlorination; however, no significant increase in HAA9 concentration was observed during chloramination. These findings are consistent with the higher reactivity of free chlorine relative to combined chlorine (Speitel et al, 1999; Zhang et al, 2000). Additionally, the magnitude of the increase in HAA9 concentration during chlorination was less than the increase observed for THM4.

Figure 4.15 shows the HAA9 concentrations for all residence times and sample dates categorized by point of entry water. The point of entry water did not appear to have an effect on the HAA9 concentrations observed in the distribution system. The increased HAA9 concentrations for the second two sample dates during chloramination (4/29/03, 5/20/03) are presumably a result of the higher temperatures (13 to 24°C) observed on these sample dates when compared to the first two sample dates during chloramination (2/11/03, 2/28/03). The magnitude of the increase in HAA9 concentrations due to temperature was not as high as the increase in THM4 concentrations. The continued increase in chlorine feed concentration as the chlorine disinfection period progressed resulted in higher HAA9 concentrations for the second chlorine sample date (3/31/03) compared to the first sample date (3/11/03).

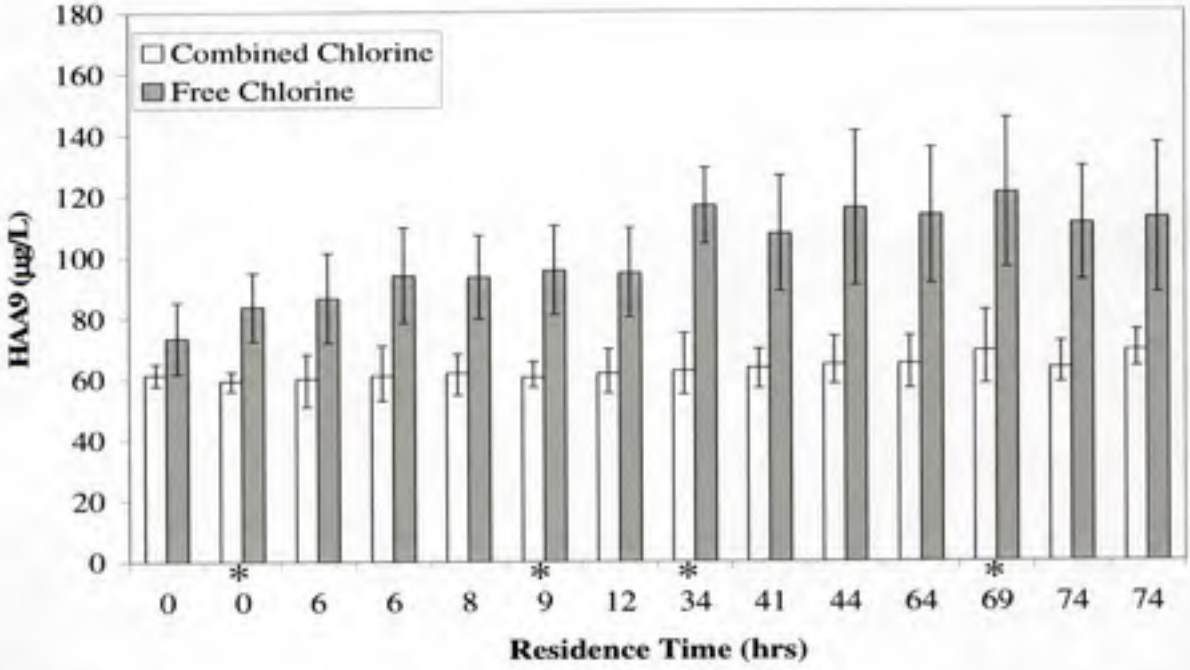

Figure 4.14 Average concentrations of HAA9 for samplings conducted while using combined chlorine or free chlorine for disinfection over the range of residence times. An asterisk indicates Site 2 point of entry water.

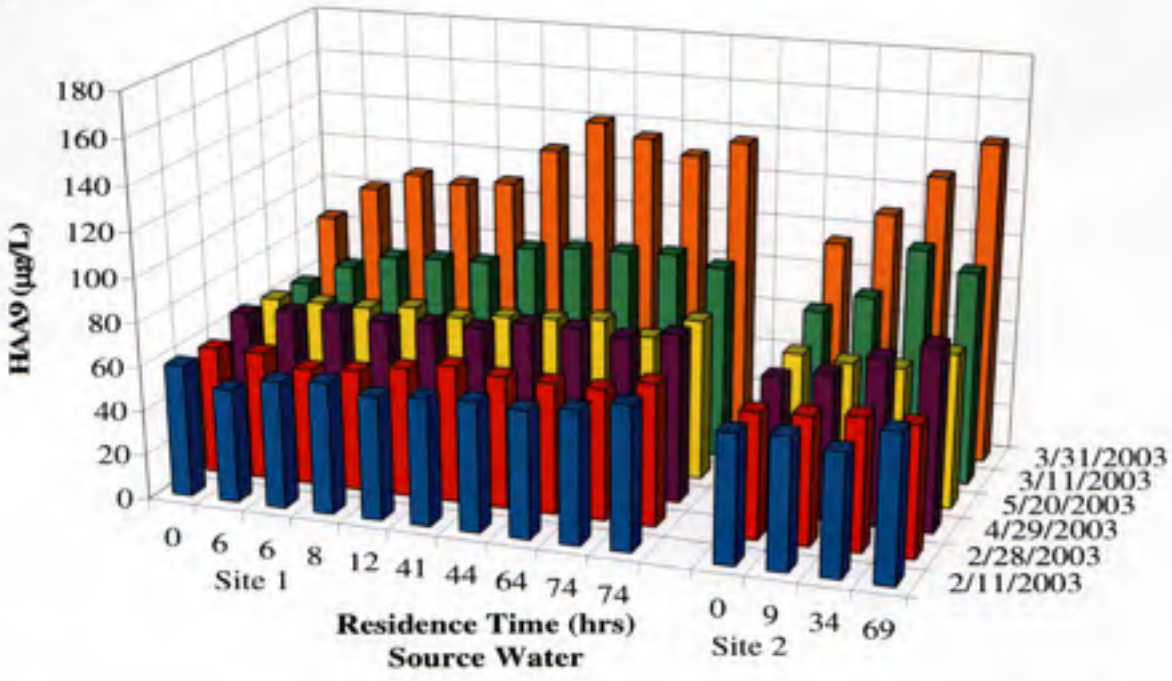

Figure 4.15 Concentrations of HAA9 over the range of residence times for all sample dates, organized by point of entry water.

Although the MCL for HAA5 of 60 µg/L is based on an annual average of four quarterly distribution system sample sites for each water treatment plant, not individual measurements, the HAA5 concentrations exceeded the MCL while using either combined chlorine or free chlorine for secondary disinfection. However, HAA5 concentrations while using free chlorine were approximately double the concentrations observed during chloramination. All distribution system samples exceeded the regulatory limit during free chlorine disinfection, regardless of temperature. HAA5 concentrations as high as 138 µg/L were observed during chlorination, which is more than twice the concentration allowed by the USEPA. The second two chloramination sample dates (4/29/03, 5/20/03), which occurred during warm water temperatures, also had HAA5 concentrations that exceeded the regulatory limit at most distribution system sample locations; however, the maximum HAA5 concentration was only 76 µg/L. Although combined chlorine disinfection limited HAA5 formation when compared to free chlorine, additional measures may be required to achieve HAA5 concentrations below the regulatory limit in Utility A's distribution system.

4.2.2.3 Comparison between THM4 and HAA9

Although THM4 and HAA9 concentrations both increased with increasing residence time in the distribution system during chlorination, the rate of formation for the two DBP classes was different. Figures 4.16 and 4.17 show the relationship between THM4 and HAA9 concentrations as residence time increases while using combined chlorine and chlorine for secondary disinfection, respectively. During chloramination, the THM4 and HAA9 concentrations remained relatively constant as residence time increased. However, the THM4 and HAA9 concentrations increased with increasing residence time in the distribution system while using free chlorine for secondary disinfection. This increase was greater for THM4, where up to 100 µg/L of THM4 were formed in the distribution system during chlorination and the concentration of THM4 formed in the distribution system was more than twice the concentration measured at the point of entry on several occasions. The comparisons of THM4 and HAA9 concentrations for all other sample dates are consistent with the observations previously described, and are presented in Appendix B.

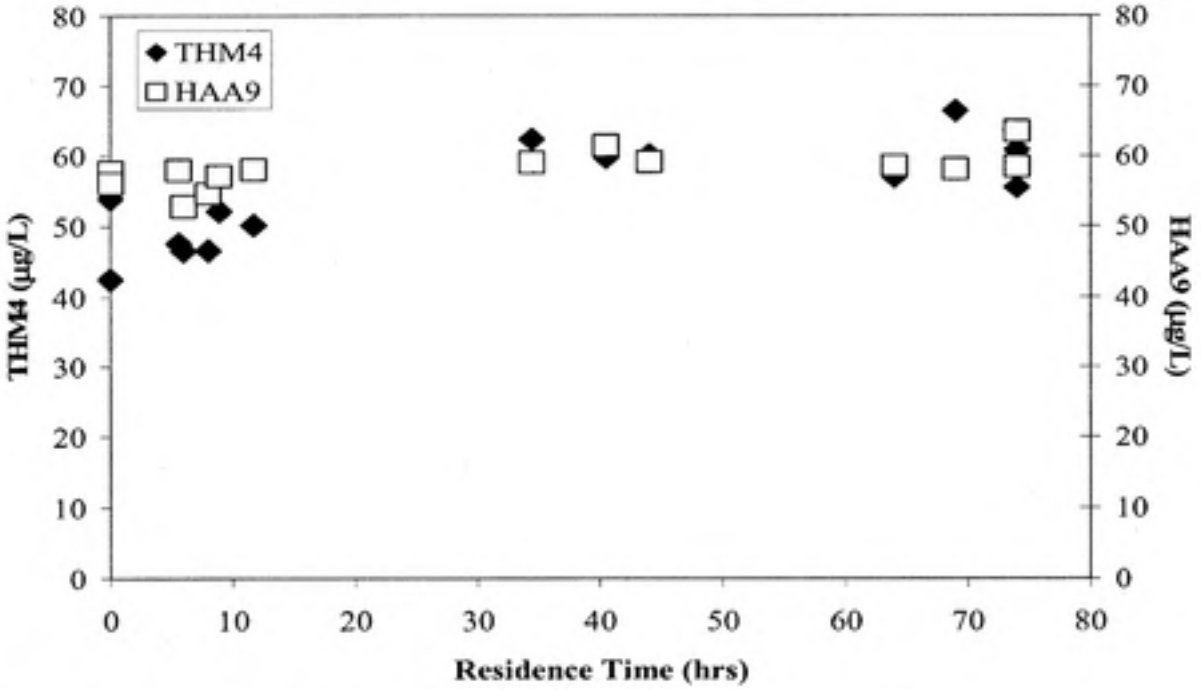

Figure 4.16 Comparison of the HAA9 and THM4 concentrations on 2/28/03 while using combined chlorine for secondary disinfection.

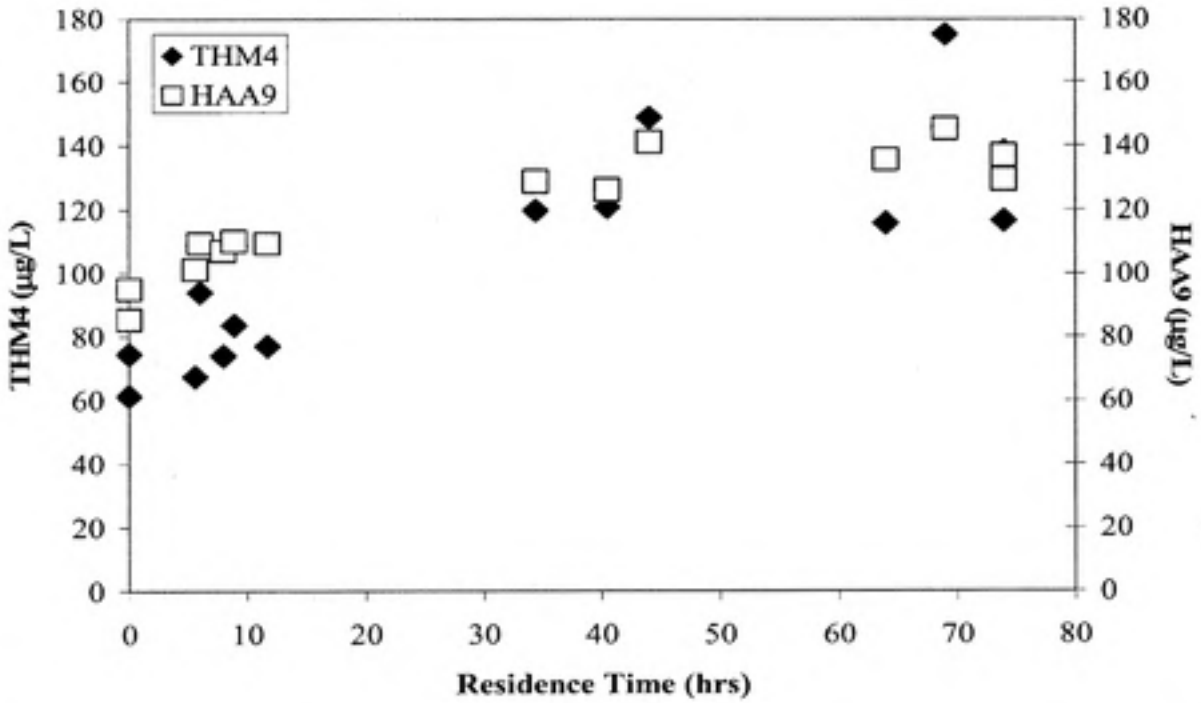

Figure 4.17 Comparison of the HAA9 and THM4 concentrations on 3/31/03 while using free chlorine for secondary disinfection.

4.2.2.4 Relationship between Free Chlorine Residual and DBPs

The free chlorine concentration in the distribution system can be correlated to DBP concentrations when free chlorine is used as the terminal disinfectant. Figures 4.18 and 4.19 present the THM4 and HAA9 concentrations for each ordered free chlorine residual on 3/31/03, respectively. A trend of increasing DBP concentration with decreasing free chlorine concentration was observed, where the increase is greater for THM4 than for HAA9. This is expected because of the higher concentrations of THM4 produced within the distribution system compared to HAA9, as discussed previously. Figure 4.20 shows the corresponding free chlorine and THM4 concentrations as residence time increases on 3/31/03. Again, a trend of increasing THM4 concentration and decreasing free chlorine residual was observed for increasing residence time. The results for 3/11/03 are presented in Appendix B, and are consistent with the observations for 3/31/03.

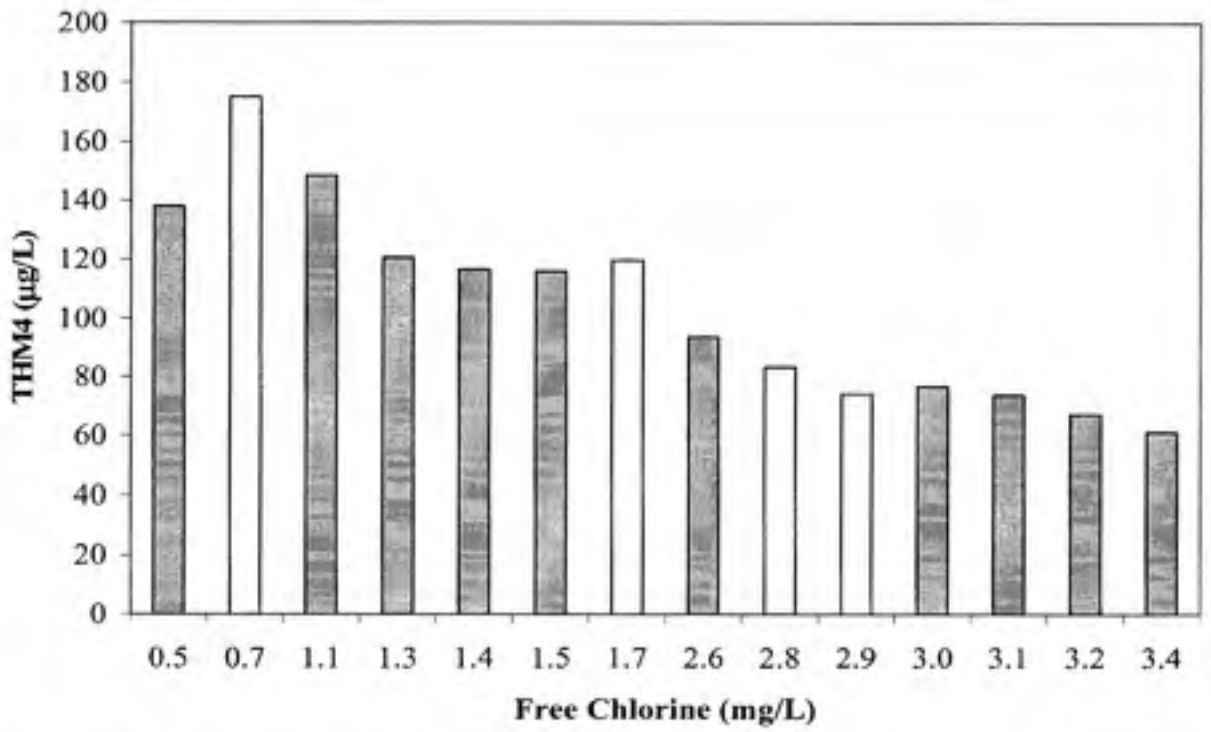

Figure 4.18 THM4 concentrations and corresponding free chlorine concentrations on 3/31/03 while using free chlorine for secondary disinfection. Sample sites receiving Site 1 point of entry water are in gray, and locations receiving Site 2 point of entry water are in white.

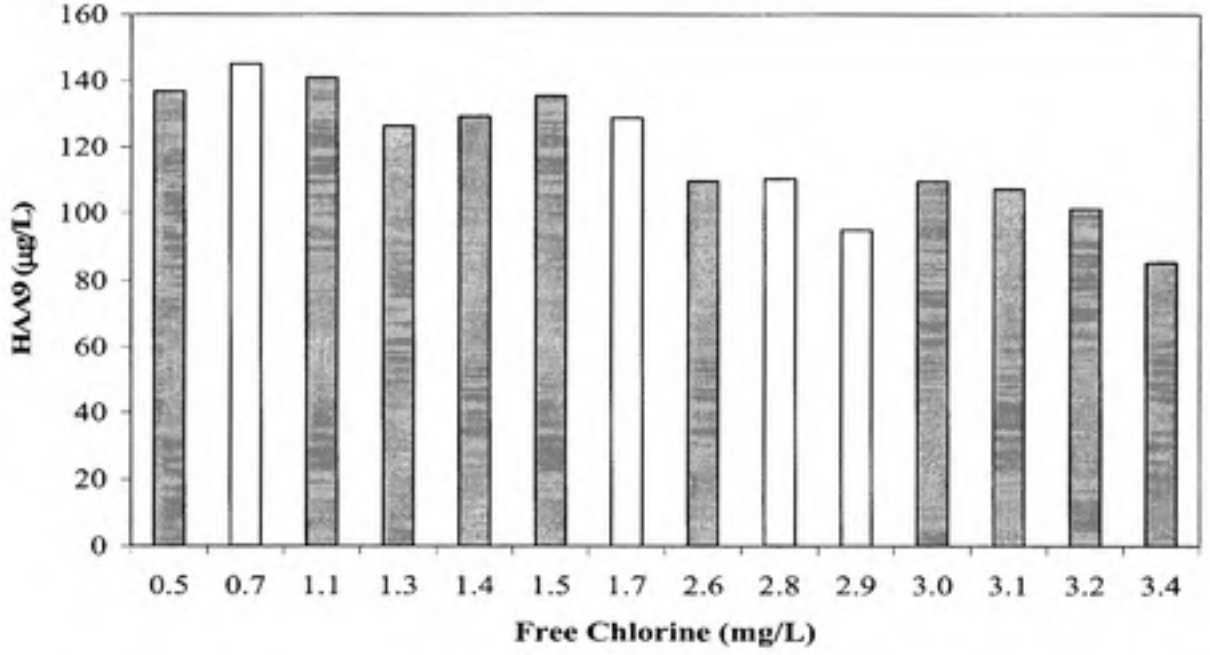

Figure 4.19 HAA9 concentrations and corresponding free chlorine concentrations on 3/31/03 while using free chlorine for secondary disinfection. Sample sites receiving Site 1 point of entry water are in gray, and locations receiving Site 2 point of entry water are in white.

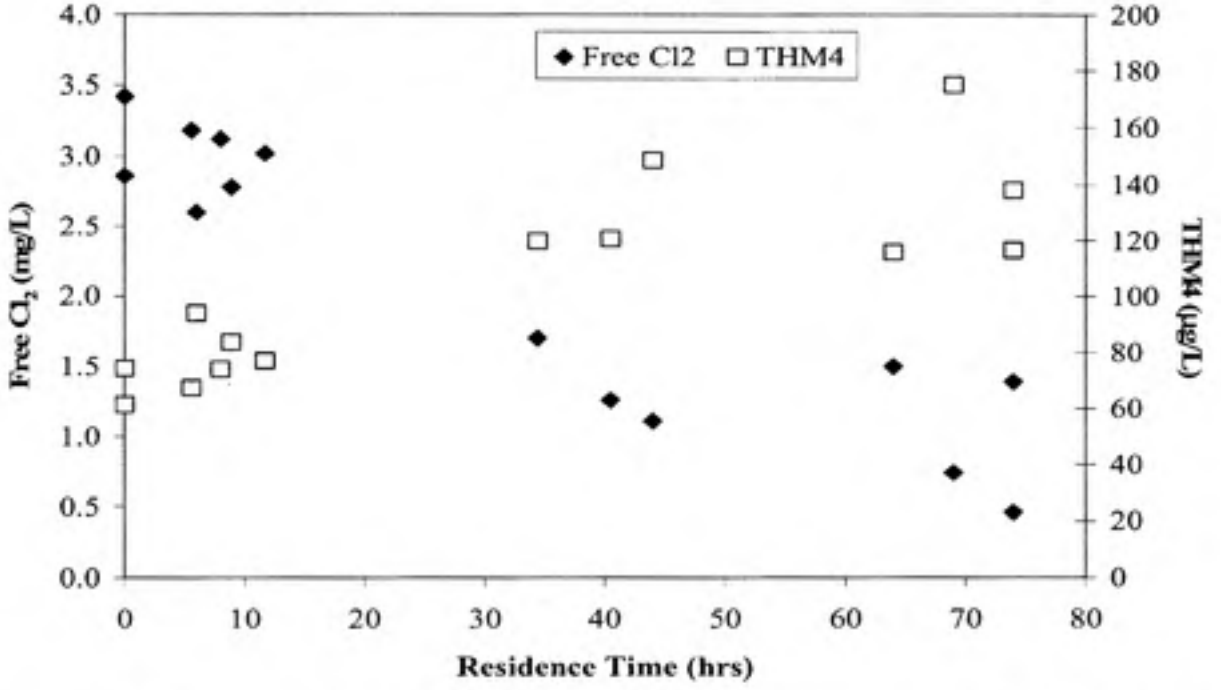

Figure 4.20 Comparison between THM4 and free chlorine concentrations for all residence times on 3/31/03 while using free chlorine for secondary disinfection.

4.2.2.5 Effect of Pipe Diameter and Pipe Material

The pipe diameter and pipe material had no discernable effect on DBP formation in the distribution system. Figures 4.21 and 4.22 are examples of THM4 and HAA9 concentrations, respectively, for different pipe diameter categories at a high residence time in ductile iron pipes receiving Site 1 point of entry water. An additional comparison of DBP concentrations by pipe diameter category at a low residence time in ductile iron pipes receiving Site 1 point of entry water is presented in Appendix B. The THM4 and HAA9 concentrations did not change as pipe diameter increased indicating that changes in the surface area to volume ratio were not significant in this distribution system during the study period. (The THM4 concentration did decrease slightly as pipe diameter increased in low residence time, ductile iron pipes receiving Site 1 point of entry water (see Appendix B), but this apparent decrease may be a result of residence time variation within the low residence time stratum.)

Figures 4.23 and 4.24 present the differences in THM4 and HAA9 concentrations, respectively, for cast and ductile iron pipe materials in low residence time, small diameter pipes receiving Site 1 point of entry water. Appendix B contains another comparison of DBP concentrations for cast and ductile iron pipes at a medium residence time in medium diameter pipes receiving Site 1 point of entry water. The DBP concentrations did not differ with pipe material for any set of conditions tested in this study.

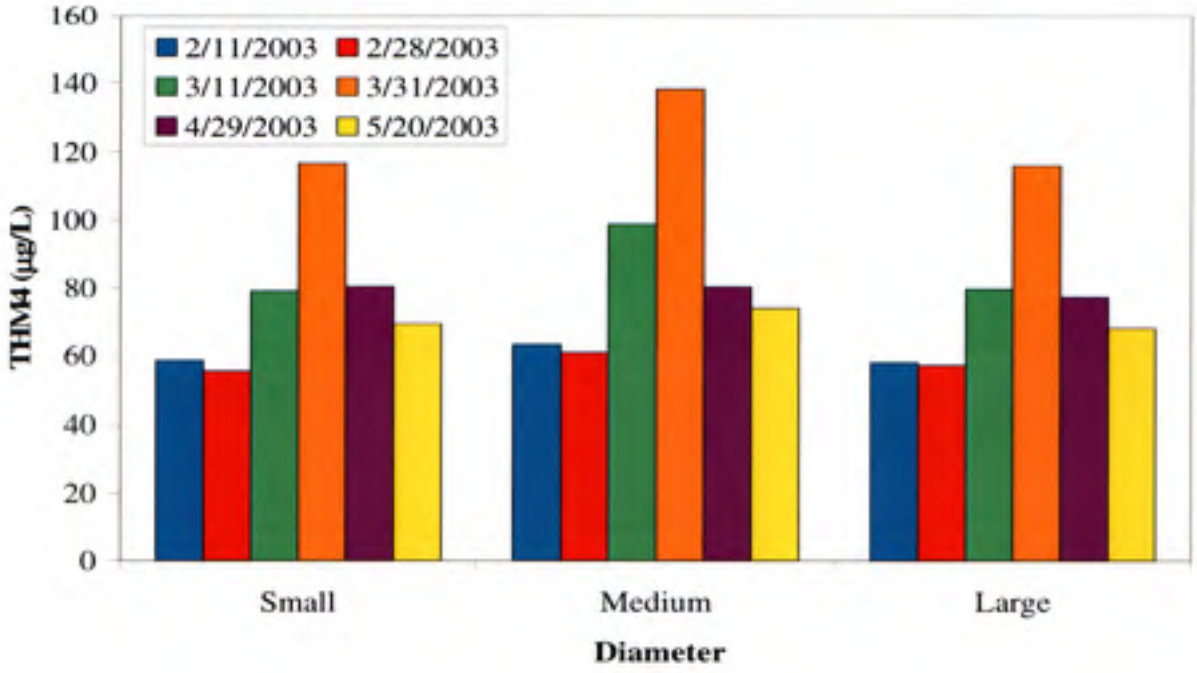

Figure 4.21 Variation in THM4 concentrations with varying pipe diameters for high residence time, ductile iron pipes receiving Site 1 point of entry water.

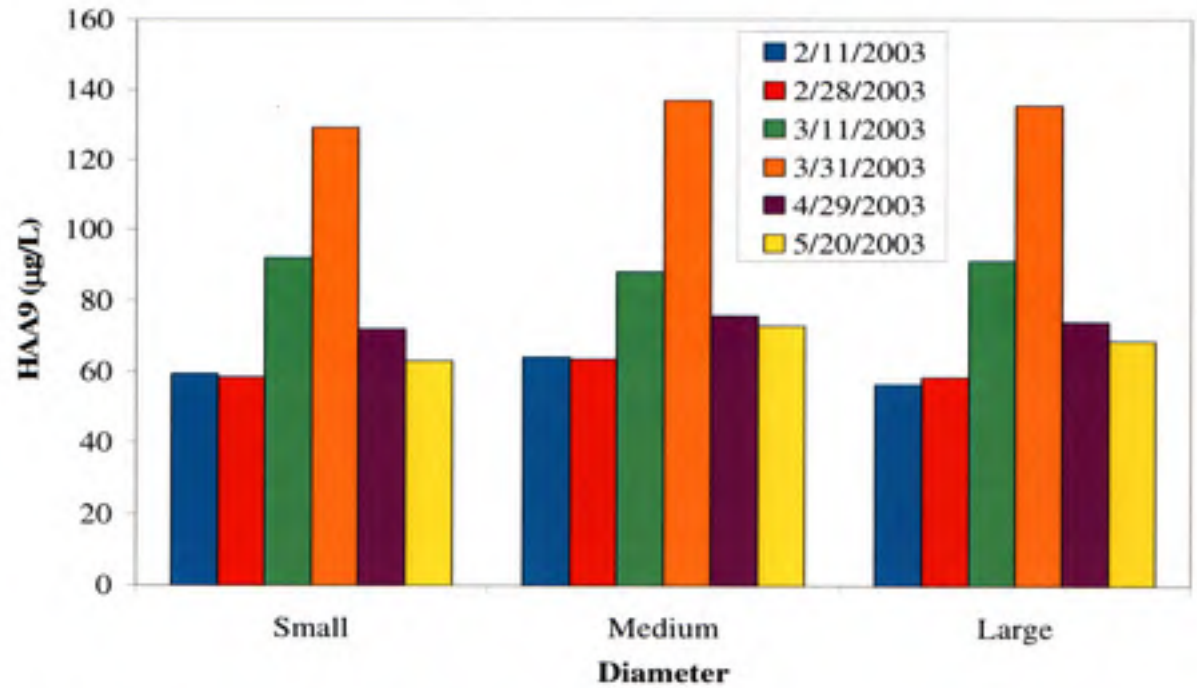

Figure 4.22 Variation in HAA9 concentration with varying pipe diameters for high residence time, ductile iron pipes receiving Site 1 point of entry water.

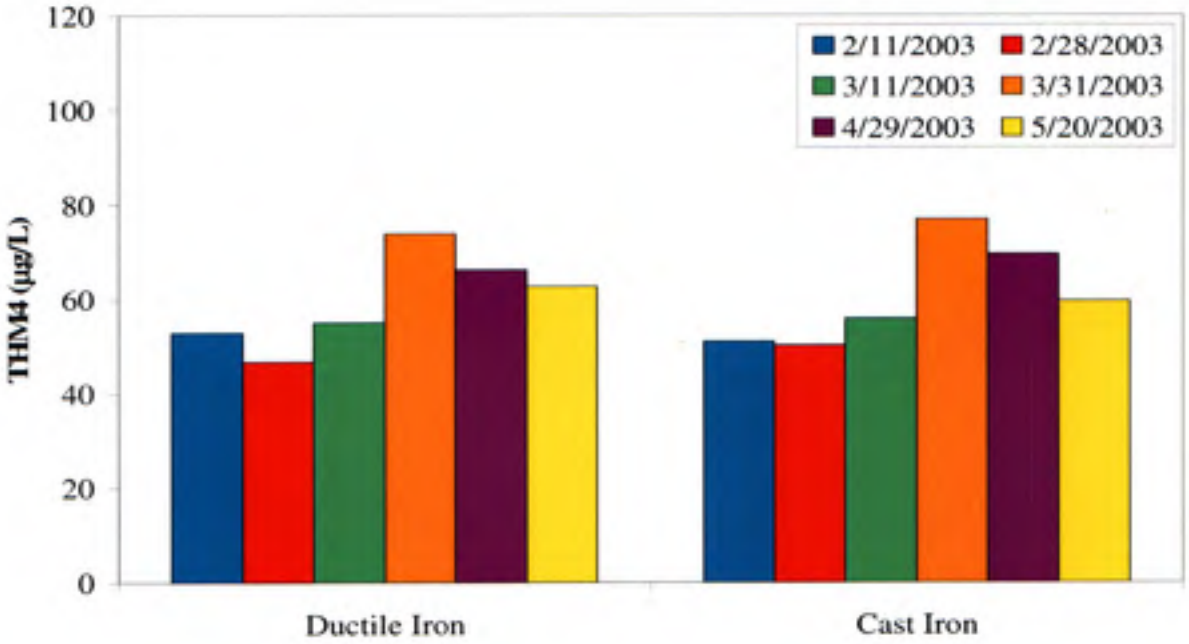

Figure 4.23 Comparison of THM4 concentrations in ductile iron and cast iron pipes for low residence time, small diameter pipes with Site 1 point of entry water.

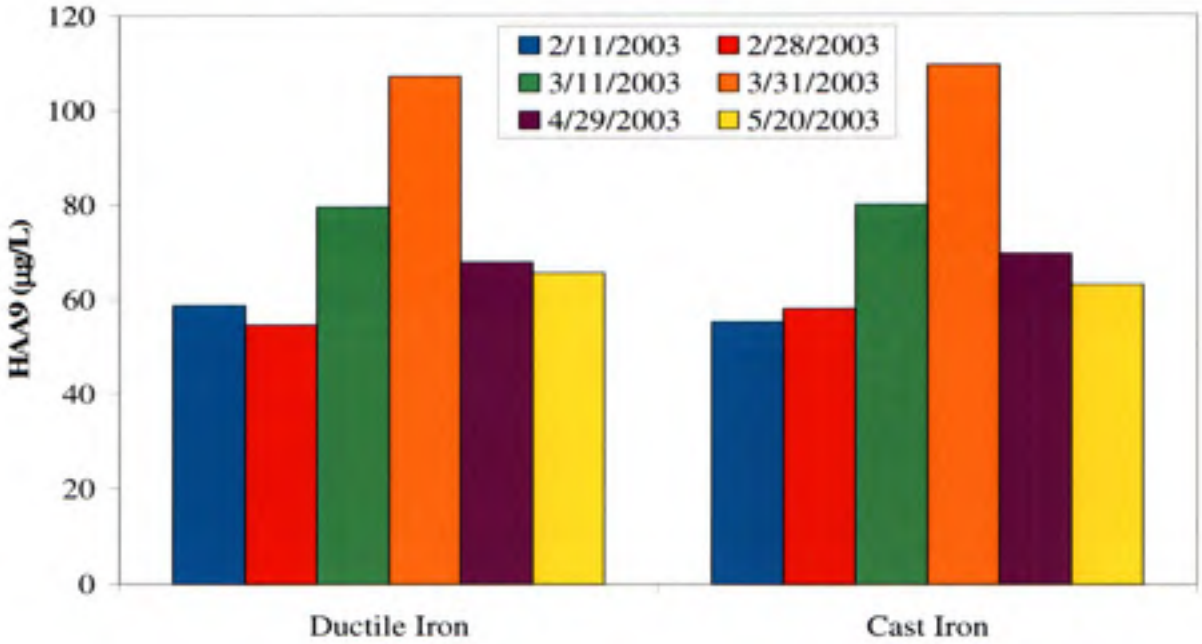

Figure 4.24 Comparison of HAA9 concentrations in ductile iron and cast iron pipes for low residence time, small diameter pipes with Site 1 point of entry water.

4.2.2.6 Biodegradation of HAAs

Biodegradation of HAAs was not observed in the distribution system under the conditions present during this study. Figures 4.25 and 4.26 present illustrative free or total chlorine residuals and HPCs for all residence times while using free chlorine or combined chlorine for secondary disinfection, respectively. The figures for the remaining sample dates are presented in Appendix B, and are consistent with the following findings. Total chlorine residuals of 2.6 mg/L or greater were maintained throughout the distribution system during chloramination, which should have been a sufficiently high concentration of monochloramine to limit the growth of bacterial populations within the distribution system (LeChevallier et al, 1990; LeChevallier et al, 1996; Momba et al, 2003).

No free chlorine residual was present at two sample locations for the first sampling conducted during chlorination (3/11/03). Although the loss of residual produced elevated HPCs during subsequent sampling (3/31/03), no decrease in HAA concentration was observed. The biodegradation of HAA9 may occur in Utility A's distribution system during prolonged warm water temperatures because of the more favorable conditions for microbial growth and disinfectant dissipation in warm water, but no samples were taken under such conditions.

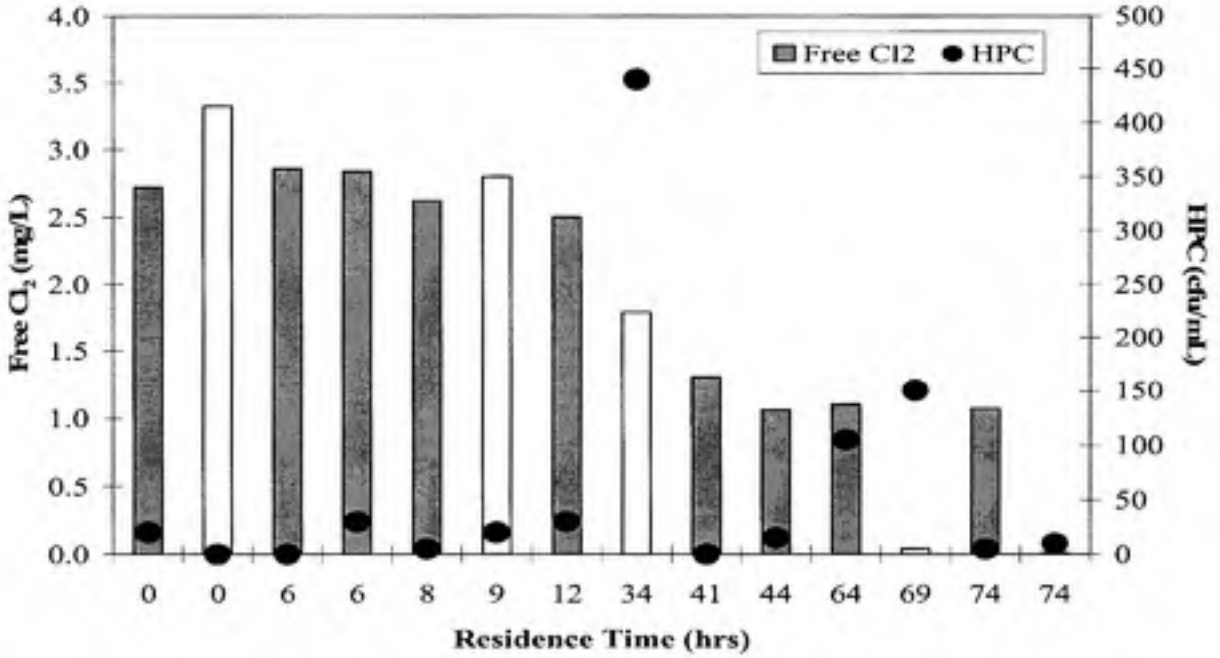

Figure 4.25 Comparison of the free chlorine concentrations and HPCs for all residence times during chlorination on 3/11/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

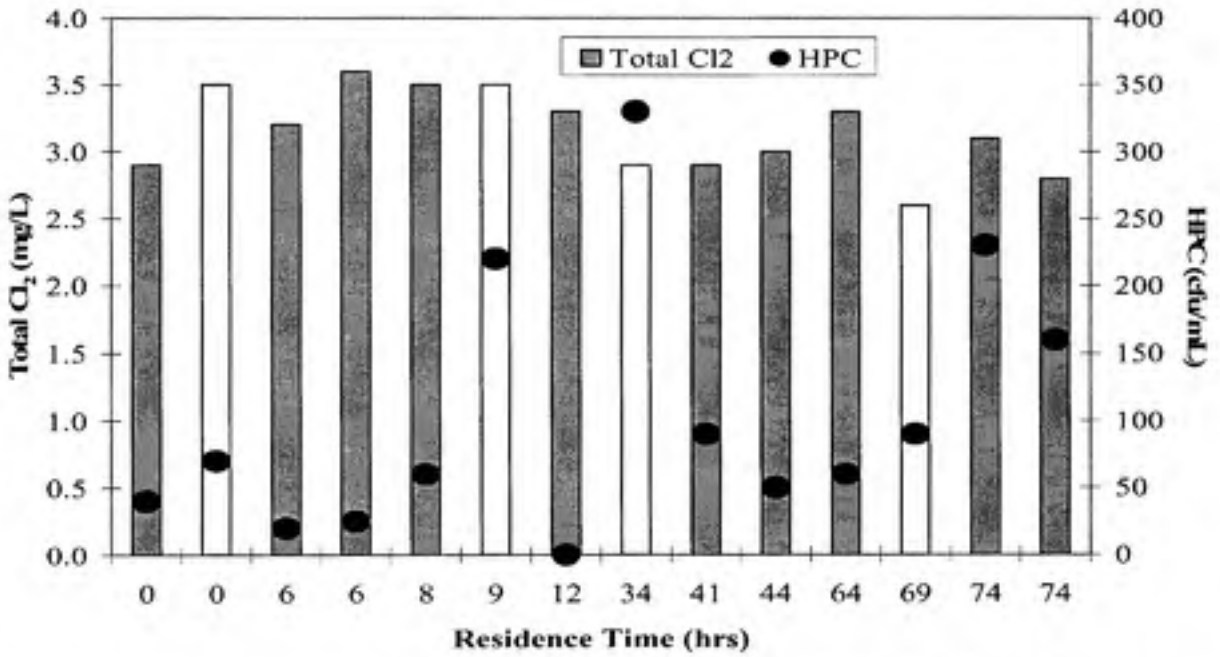

Figure 4.26 Comparison of the total chlorine concentrations and HPCs for all residence times during chloramination on 5/20/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

4.2.2.7 Batch Kinetic Testing

Batch kinetic testing was conducted on several sample dates to determine the effect of pipe wall demands on disinfectant decay and DBP formation. Batch samples were collected from one of the point of entry locations, and stored at the water temperature measured during sample collection. Samples were taken from the bottles at 24, 48, and 72 hours for DBP analysis. The results are presented in Appendix C. A general trend of decreasing disinfectant concentration with increasing holding time was observed for both disinfectants. However, the decreases in concentration were relatively small when compared to parallel samples taken from the distribution system. The THM4 and HAA9 concentrations remained relatively constant with increasing residence time for both disinfectants tested. DBP formation in the presence of combined chlorine was not expected to change significantly, but DBP concentrations in the presence of a free chlorine residual were expected to increase (Rossman et al, 2001). The reason for the stability of the free chlorine residual and the corresponding DBP concentrations in these tests are not known. One possible reason is that organic material is the limiting reactant for DBP formation in the bulk phase in this system.

4.3 SUMMARY

Figures 4.27 and 4.28 present the THM4 and HAA9 concentrations, respectively, along with HPCs, organized by free chlorine residual during the use of free chlorine on 3/11/03. The residence time associated with each free chlorine concentration is listed above each bar. Figures for 3/31/03 are in Appendix C, and are consistent with the following observations. The concentration of both DBPs increased with decreasing free chlorine residual; however, the effect was much greater for THM4 than for HAA9. In general, the free chlorine concentration decreased and the DBP concentration increased with increasing residence time in the distribution system. The HPCs were less than 200 cfu/mL at all sample locations while using free chlorine for secondary disinfection, with the exception of Site 4 (34 hrs) on 3/11/03. Even in the absence of a free chlorine residual, HPCs were less than 200 cfu/mL and no biodegradation was apparent.

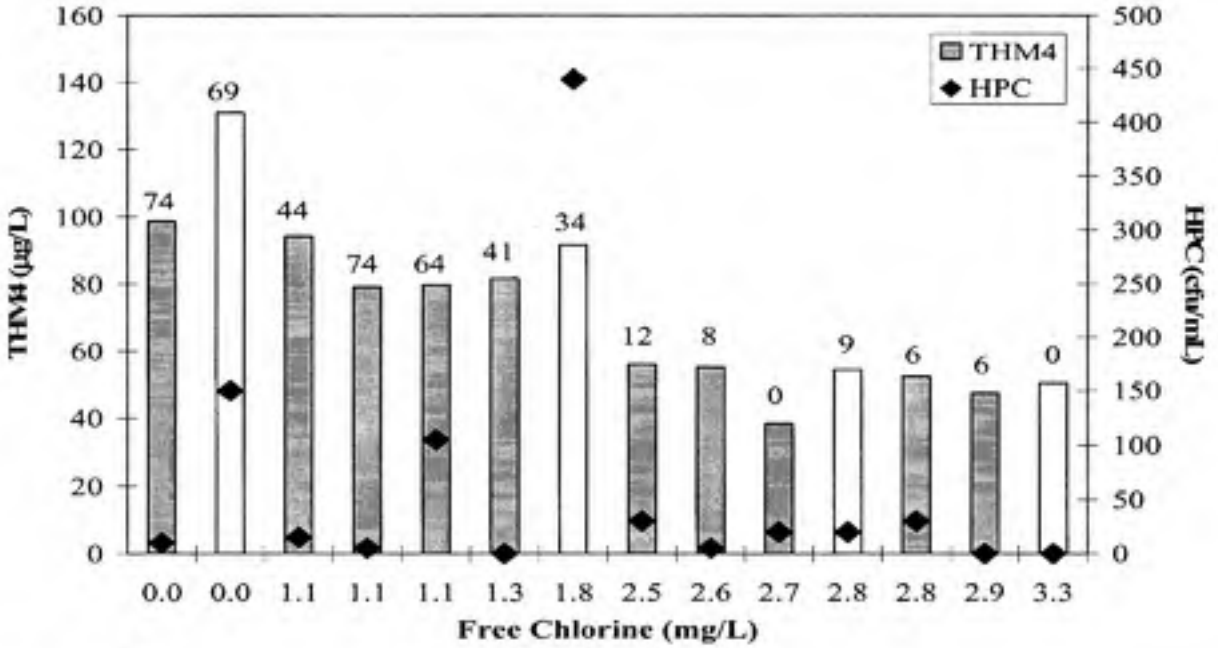

Figure 4.27 Comparison among THM4, HPC, and free chlorine concentrations during chlorination on 3/11/03. Residence times are listed above each bar. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

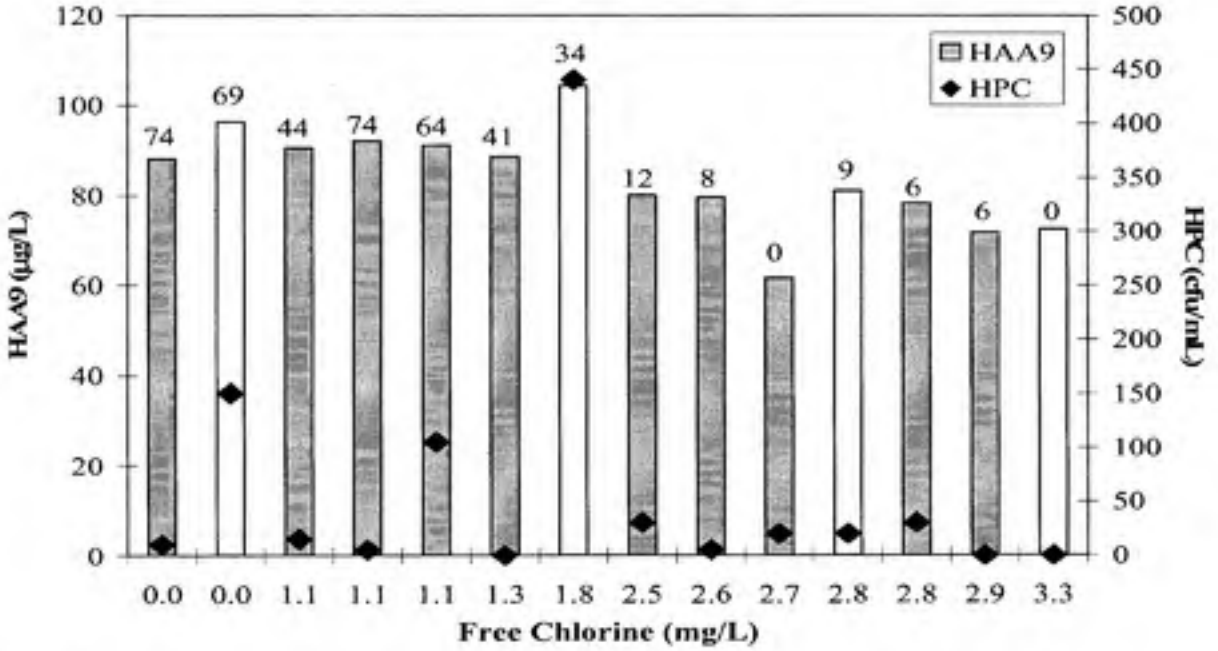

Figure 4.28 Comparison among HAA9, HPC, and free chlorine concentrations during chlorination on 3/11/03. Residence times are listed above each bar. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

Figures 4.29 and 4.30 show the THM4 and HAA9 concentrations, respectively, along with the HPCs for all residence times while using combined chlorine for secondary disinfection on 5/20/03. The figures for all other sample dates during chloramination are presented in Appendix B. The THM4 concentration increased slightly with increasing residence time in the distribution system, while the HAA9 concentration remained essentially constant. HPCs were generally below 350 cfu/mL during chloramination; however, an HPC of 675 cfu/mL was observed at Site 4 (34 hrs) on 4/29/03. No trend between residence time and HPCs were observed during secondary disinfection with combined chlorine in this study.

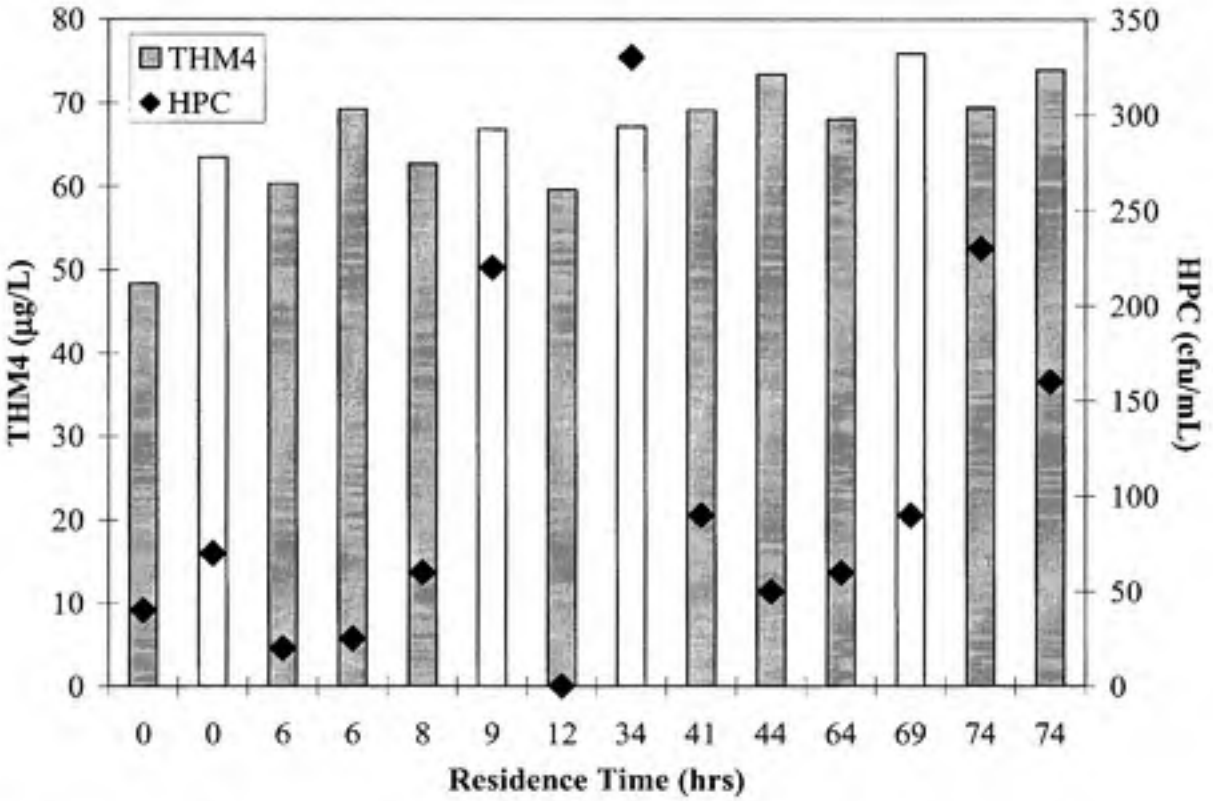

Figure 4.29 Comparison between THM4 concentrations and HPCs for all residence times during chloramination on 5/20/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

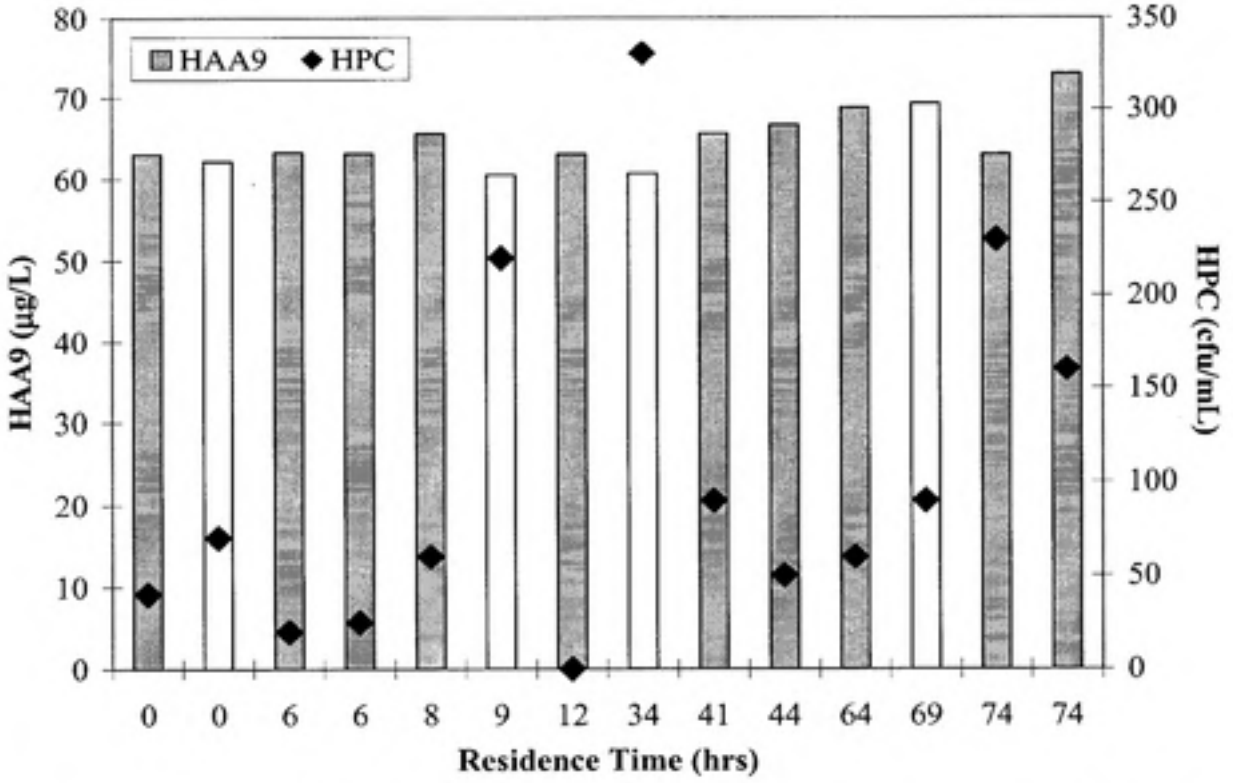

Figure 4.30 Comparison between HAA9 concentrations and HPCs for all residence times during chloramination on 5/20/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The primary objective of this study was to evaluate the formation and decay of THMs and HAAs in a full-scale distribution system while the utility switched the secondary disinfectant from combined chlorine to free chlorine for a one-month period, and then back to combined chlorine. In addition, changes in nitrogen species and HPCs were measured before, during, and after the switch in disinfectants. To fully characterize the changes in the distribution system during each phase of the study, 14 distribution system sample sites were chosen that presented a wide range of possible point of use attributes. The water ages were estimated using the EPANET distribution system model, and appear to be consistent with the data collected for most sampling locations. The analyses of these samples resulted in the following conclusions:

1. Free chlorine dissipated in the distribution system proportionally to residence time, while the combined chlorine residual was more stable. Free chlorine continued to react with organic and inorganic matter in the distribution system resulting in increased DBP concentrations and decreased disinfectant residuals. Pipe diameter and pipe material had no discernable effect on free chlorine decay.
2. Use of free chlorine for secondary disinfection produced significantly higher DBP concentrations than combined chlorine. DBP concentrations were relatively consistent throughout the distribution system during chloramination, but continued to increase with increasing residence time during chlorination. The THM concentration increased to a greater extent than the HAA concentration as residence time increased. Pipe diameter and pipe material had no observable effect on the THM or HAA concentrations.
3. No biological degradation of HAAs was observed during this study. The possible causes for the lack of HAA degradation include the high combined chlorine residual maintained throughout the distribution system during chloramination, the short time period during which free chlorine was used for secondary disinfection, the limited number of sites with no detectable free chlorine residual during chlorination, and the low water temperatures during the period of observation.

4. Nitrification was not observed in the distribution system based on measurements of nitrogen species concentrations and the overall low HPCs. The ammonia concentration dropped from the point of entry to sample sites within the distribution system on several occasions; however, this drop was not associated with an increase in nitrite or nitrate concentrations.
5. HPCs were unaffected by the switch from combined chlorine to free chlorine. However, lower HPCs were observed during this study while using combined chlorine for secondary disinfection when compared to historical data collected while free chlorine was used year-round for secondary disinfection. Relatively high HPCs were observed in some instances at sites with disinfectant concentrations greater than 3 mg/L. Pipe diameter and pipe material had no significant impact on HPCs measured during this study.

5.2 RECOMMENDATIONS

The recently proposed Stage 2 D/DBP Rule will significantly affect how many United States utilities treat and distribute drinking water. Each water utility will need to fully assess their ability to meet the proposed regulations by identifying the points of maximum THM and HAA concentrations in their distribution system. Research has indicated that the maximum residence time locations will provide the highest THM concentrations in the distribution system; however, HAA concentrations may be higher at mid-points within the distribution system due to biological degradation of HAAs at the sites with high residence times and low disinfectant residuals. Changes in sample locations and the method of averaging sample concentrations may bring some utilities out of compliance. Conducting sampling throughout Utility A's distribution system during the warmest months may identify the maximum HAA concentrations at locations other than the maximum residence time locations. A tool to assist utilities in determining the points of maximum THM and HAA concentrations is currently being developed in preparation for the final Stage 2 D/DBP Rule, and should prove useful to Utility A.

In addition, "significant excursions" are a concern utilities will be forced to address with the proposed new regulation. In the case of Utility A, the maximum DBP concentrations measured while free chlorine was the secondary disinfectant were more than double the

concentrations observed when combined chlorine was used. This may be considered a "significant excursion" in the future, requiring the amendment of State regulations or drinking water treatment and distribution practices. Short-term temporal changes in DBP concentrations were not investigated during this study; however, such changes may become important as future regulations attempt to eliminate high exposures to DBPs.

A statistical analysis of the key parameters investigated in this report using the analysis of variance (ANOVA) procedure is recommended. This would identify the statistically significant variables that impact the DBP concentrations in Utility A's distribution system. This investigation was not designed to allow for such an analysis. To achieve accurate results from an ANOVA analysis, the sample size would need to be increased. Additional sampling would also broaden the range of conditions under which the distribution system is analyzed.

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Appendix A

Chemical and Biological Data

Table A.1

Sample site parameters and on-site data for 2/11/03, while using combined chlorine.

	Site Parameters			On-Site Data			
Sample ID	Pipe Diameter (in)	Pipe Material	Residence Time (hrs)	Temperature (°C)	pH	Free Cl_2 (mg/L)	Total Cl_2 (mg/L)
Site 1	-	-	0	6.4	8.0	0.11	3.5
Site 2	-	-	0	9.0	8.7	0.18	3.6
Site 3	12	D	74	12.3	9.0	0.11	3.4
Site 4	12	D	34	12.7	9.4	0.06	3.1
Site 5	4	D	41	11.0	9.2	0.21	3.3
Site 6	6	C	44	8.2	8.8	0.04	2.9
Site 7	2	C	9	12.9	8.8	0.31	3.4
Site 8	4	D	6	8.3	8.5	0.04	3.0
Site 9	8	D	8	7.2	8.5	0.04	3.1
Site 10	16	D	6	6.5	8.0	0.08	3.1
Site 11	12	D	69	14.0	8.2	0.09	3.1
Site 12	8	D	74	10.8	8.9	0.10	2.9
Site 13	8	C	12	6.8	8.5	0.07	3.3
Site 14	4	D	64	9.6	8.3	0.11	3.1

Table A.2

Sample site parameters and on-site data for 2/28/03, while using combined chlorine.

	Site Parameters			On-Site Data			
Sample ID	Pipe Diameter (in)	Pipe Material	Residence Time (hrs)	Temperature (°C)	pH	Free Cl_2 (mg/L)	Total Cl_2 (mg/L)
Site 1	-	-	0	7.0	9.43	0.17	3.4
Site 2	-	-	0	8.0	8.73	0.11	4.7
Site 3	12	D	74	9.1	9.38	0.15	3.1
Site 4	12	D	34	12.2	8.9	0.13	3.3
Site 5	4	D	41	10.1	9.13	0.14	3.1
Site 6	6	C	44	9.0	8.73	0.12	3.0
Site 7	2	C	9	11.0	8.7	0.15	3.6
Site 8	4	D	6	9.0	8.25	0.16	3.1
Site 9	8	D	8	7.0	8.21	0.21	3.5
Site 10	16	D	6	7.0	8.35	0.17	3.1
Site 11	12	D	69	9.0	8.39	0.08	3.8
Site 12	8	D	74	11.0	8.66	0.12	2.9
Site 13	8	C	12	7.0	8.72	0.23	3.4
Site 14	4	D	64	10.0	8.51	0.12	3.0

Table A.3

Sample site parameters and on-site data for 3/11//03, while using free chlorine.

	Site Parameters			On-Site Data			
Sample ID	Pipe Diameter (in)	Pipe Material	Residence Time (hrs)	Temperature (°C)	pH	Free Cl_2 (mg/L)	Total Cl_2 (mg/L)
Site 1	-	-	0	9.9	7.4	2.72	3.0
Site 2	-	-	0	10.2	7.0	3.32	3.4
Site 3	12	D	74	11.5	6.5	0.04	0.2
Site 4	12	D	34	12.3	7.7	1.79	2.1
Site 5	4	D	41	12.0	6.5	1.06	1.2
Site 6	6	C	44	10.5	6.9	1.30	1.4
Site 7	2	C	9	11.1	6.9	2.80	3.0
Site 8	4	D	6	10.9	6.9	2.84	2.9
Site 9	8	D	8	9.9	6.9	2.62	2.9
Site 10	16	D	6	9.7	6.9	2.86	3.2
Site 11	12	D	69	17.5	6.9	1.10	1.3
Site 12	8	D	74	12.5	6.9	0.01	0.1
Site 13	8	C	12	9.7	7.0	2.50	3.1
Site 14	4	D	64	11.1	7.0	1.07	1.2

Table A.4

Sample site parameters and on-site data for 4/29//03, while using combined chlorine.

	Site Parameters			On-Site Data			
Sample ID	Pipe Diameter (in)	Pipe Material	Residence Time (hrs)	Temperature (°C)	pH	Free Cl_2 (mg/L)	Total Cl_2 (mg/L)
Site 1	-	-	0	15.6	6.9	0.23	3.7
Site 2	-	-	0	15.5	7.4	0.34	3.4
Site 3	12	D	74	18.4	8.7	0.27	2.9
Site 4	12	D	34	17.1	8.4	0.10	3.2
Site 5	4	D	41	18.3	8.7	0.12	3.1
Site 6	6	C	44	17.6	8.3	0.31	3.0
Site 7	2	C	9	17.3	7.4	0.13	3.6
Site 8	4	D	6	18.8	8.4	0.18	3.8
Site 9	8	D	8	16.0	7.8	0.12	2.9
Site 10	16	D	6	19.6	7.7	0.10	2.9
Site 11	12	D	69	15.6	8.2	0.14	3.3
Site 12	8	D	74	19.4	8.4	0.21	2.9
Site 13	8	C	12	16.2	8.2	0.38	-
Site 14	4	D	64	17	8.3	0.14	3.0

Table A.5

Point of entry measurements, nitrogen species, and heterotrophic plate counts for 2/11/03, while using combined chlorine.

Sample ID	UV 254 (cm^{-1})	TOC (mg/L)	AOC (µg/L)	Nitrogen Species (mg/L)			HPC (cfu/mL)
				NH_3	NO_2^-	NO_3^-	
Site 1	0.046	2.20	193	0.26	<0.1	0.4	10
Site 2	0.050	2.22	-	0.23	<0.1	0.4	< 10
Site 3	-	-	-	0.12	<0.1	0.4	5
Site 4	-	-	-	0.31	<0.1	0.3	220
Site 5	-	-	-	0.36	<0.1	0.4	20
Site 6	-	-	-	0.34	<0.1	0.4	5
Site 7	-	-	-	0.28	<0.1	0.3	105
Site 8	-	-	-	0.20	<0.1	0.4	< 10
Site 9	-	-	-	0.23	<0.1	0.4	20
Site 10	-	-	-	0.22	<0.1	0.4	< 10
Site 11	-	-	-	0.32	<0.1	0.4	20
Site 12	-	-	-	0.24	<0.1	0.4	25
Site 13	-	-	-	0.22	<0.1	0.4	15
Site 14	-	-	-	0.31	<0.1	0.4	< 10

Table A.6

Point of entry measurements and nitrogen species for 2/28/03, while using combined chlorine.

Sample ID	UV 254 (cm^{-1})	TOC (mg/L)	NH_3 (mg/L)	AOC (mg/L)
Site 1	0.046	1.81	0.64	519
Site 2	0.049	2.12	0.49	361
Site 3	-	-	0.59	-
Site 4	-	-	0.62	-
Site 5	-	-	0.61	-
Site 6	-	-	0.64	-
Site 7	-	-	0.58	-
Site 8	-	-	0.51	-
Site 9	-	-	0.46	-
Site 10	-	-	0.51	-
Site 11	-	-	0.63	-
Site 12	-	-	0.67	-
Site 13	-	-	0.72	-
Site 14	-	-	0.62	-

Table A.7

Point of entry measurements, nitrogen species, and heterotrophic plate counts for 3/11/03, while using free chlorine.

Sample ID	UV 254 (cm^{-1})	TOC (mg/L)	Nitrogen Species (mg/L)			HPC (cfu/mL)
			NH_3	NO_2^-	NO_3^-	
Site 1	0.026	2.01	<0.05	<0.1	0.3	20
Site 2	0.031	2.55	<0.05	<0.1	0.3	<10
Site 3	-	-	<0.05	<0.1	0.3	150
Site 4	-	-	<0.05	<0.1	0.3	440
Site 5	-	-	0.08	<0.1	0.3	15
Site 6	-	-	<0.05	<0.1	0.3	<10
Site 7	-	-	<0.05	<0.1	0.3	20
Site 8	-	-	<0.05	<0.1	0.3	30
Site 9	-	-	<0.05	<0.1	0.3	5
Site 10	-	-	<0.05	<0.1	0.3	<10
Site 11	-	-	<0.05	<0.1	0.4	105
Site 12	-	-	<0.05	<0.1	0.4	10
Site 13	-	-	<0.05	<0.1	0.3	30
Site 14	-	-	<0.05	<0.1	0.3	5

Table A.8

Point of entry measurements, nitrogen species, and heterotrophic plate counts for 4/29/03, while using combined chlorine.

Sample ID	UV 254 (cm^{-1})	TOC (mg/L)	AOC (µg/L)	Nitrogen Species (mg/L)			HPC (cfu/mL)
				NH_3	NO_2^-	NO_3^-	
Site 1	0.044	1.57	204	0.08	<0.1	0.2	<10
Site 2	0.049	1.95	198	0.22	<0.1	0.2	10
Site 3	-	-	-	0.23	<0.1	0.2	675
Site 4	-	-	-	0.21	<0.1	0.2	115
Site 5	-	-	-	0.15	<0.1	0.2	15
Site 6	-	-	-	0.18	<0.1	0.2	30
Site 7	-	-	-	0.15	<0.1	0.2	25
Site 8	-	-	-	0.09	<0.1	0.2	70
Site 9	-	-	-	0.06	<0.1	0.2	<10
Site 10	-	-	-	0.06	<0.1	0.2	50
Site 11	-	-	-	0.14	<0.1	0.2	15
Site 12	-	-	-	0.14	<0.1	0.2	110
Site 13	-	-	-	0.15	<0.1	0.2	<10
Site 14	-	-	-	0.12	<0.1	0.2	<10

Table A.9

Trihalomethane concentrations (µg/L) for 2/11/03, while using combined chlorine.

Sample ID	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	THM4
Site 1	31.9	5.2	<1	<1	37.1
Site 2	40.2	6.6	<1	<1	46.8
Site 3	62.8	7.5	<1	<1	70.3
Site 4	53.5	7.7	<1	<1	61.3
Site 5	56.0	7.3	<1	<1	63.3
Site 6	52.1	7.1	<1	<1	59.1
Site 7	46.2	6.9	<1	<1	53.1
Site 8	43.3	6.1	<1	<1	49.4
Site 9	46.3	6.5	<1	<1	52.8
Site 10	40.7	6.0	<1	<1	46.8
Site 11	51.0	6.8	<1	<1	57.8
Site 12	56.3	6.8	<1	<1	63.1
Site 13	44.6	6.4	<1	<1	50.9
Site 14	51.4	7.1	<1	<1	58.5

Table A.10

Trihalomethane concentrations (µg/L) for 2/28/03, while using combined chlorine.

Sample ID	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	THM4
Site 1	36.3	6.2	<1	<1	42.5
Site 2	46.9	7.0	<1	<1	53.8
Site 3	58.4	8.0	<1	<1	66.4
Site 4	54.4	8.0	<1	<1	62.4
Site 5	52.5	7.5	<1	<1	60.1
Site 6	52.0	7.7	<1	<1	59.7
Site 7	45.3	6.9	<1	<1	52.1
Site 8	40.0	6.5	<1	<1	46.5
Site 9	39.9	6.6	<1	<1	46.6
Site 10	40.8	6.8	<1	<1	47.5
Site 11	49.6	7.4	<1	<1	57.0
Site 12	53.4	7.4	<1	<1	60.8
Site 13	43.3	6.9	<1	<1	50.1
Site 14	48.1	7.3	<1	<1	55.4

Table A.11

Trihalomethane concentrations (µg/L) for 3/11/03, while using free chlorine.

Sample ID	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	THM4
Site 1	32.7	5.6	<1	<1	38.3
Site 2	44.5	5.7	<1	<1	50.2
Site 3	118	12.9	<1	<1	131
Site 4	81.6	10.0	<1	<1	91.6
Site 5	82.7	11.5	<1	<1	94.1
Site 6	70.7	10.9	<1	<1	81.6
Site 7	47.2	7.1	<1	<1	54.3
Site 8	44.3	7.9	<1	<1	52.2
Site 9	46.6	8.4	<1	<1	55.0
Site 10	39.4	7.8	<1	<1	47.3
Site 11	67.1	12.5	<1	<1	79.6
Site 12	86.0	12.7	<1	<1	98.7
Site 13	47.0	8.9	<1	<1	55.8
Site 14	68.6	10.6	<1	<1	79.1

Table A.12

Trihalomethane concentrations (µg/L) for 4/29/03, while using combined chlorine.

Sample ID	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	THM4
Site 1	48.6	6.1	<1	<1	54.8
Site 2	57.8	5.7	<1	<1	63.5
Site 3	80.7	5.9	<1	<1	86.5
Site 4	75.9	6.1	<1	<1	82.0
Site 5	72.4	6.1	<1	<1	78.5
Site 6	69.5	7.2	<1	<1	76.7
Site 7	64.8	6.3	<1	<1	71.1
Site 8	65.2	7.1	<1	<1	72.3
Site 9	59.0	7.1	<1	<1	66.1
Site 10	57.6	6.8	<1	<1	64.4
Site 11	71.1	6.1	<1	<1	77.3
Site 12	74.4	6.0	<1	<1	80.4
Site 13	62.5	7.0	<1	<1	69.5
Site 14	73.7	6.8	<1	<1	80.6

Table A.13

Haloacetic acid concentrations (µg/L) for 2/11/03, while using combined chlorine.

Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
Site 1	6.0	<2	23.8	<2	24.4	<2	5.1	<2	<2	59.4
Site 2	4.9	<2	23.1	2.1	23.1	<2	4.5	<2	<2	57.5
Site 3	9.1	<2	28.0	<2	24.3	<2	4.4	<2	<2	65.7
Site 4	5.1	<2	22.9	<2	22.3	<2	4.4	<2	<2	54.7
Site 5	5.4	<2	25.3	<2	23.3	<2	4.1	<2	<2	58.0
Site 6	5.8	<2	22.9	<2	23.5	<2	4.5	<2	<2	56.7
Site 7	7.4	<2	22.4	<2	23.2	<2	5.5	<2	<2	58.7
Site 8	7.8	<2	21.5	<2	22.9	<2	4.6	<2	<2	56.9
Site 9	8.1	<2	21.3	<2	23.9	<2	5.4	<2	<2	58.8
Site 10	2.7	<2	22.0	<2	21.9	<2	4.2	<2	<2	50.9
Site 11	4.9	<2	24.4	<2	23.2	<2	4.1	<2	<2	56.6
Site 12	7.2	<2	28.1	<2	24.6	<2	4.3	<2	<2	64.1
Site 13	4.7	<2	22.3	<2	23.4	<2	4.8	<2	<2	55.1
Site 14	5.6	<2	24.2	<2	25.0	<2	4.6	<2	<2	59.4

Table A.14

Haloacetic acid concentrations (µg/L) for 2/28/03, while using combined chlorine.

Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
Site 1	6.1	<2	21.7	2.6	20.8	<2	4.6	2.0	<2	57.7
Site 2	5.8	<2	22.7	2.5	20.8	<2	4.2	<2	<2	56.0
Site 3	6.0	<2	25.3	2.7	20.4	<2	3.7	<2	<2	58.1
Site 4	7.3	<2	23.5	2.7	21.5	<2	4.1	<2	<2	59.0
Site 5	8.2	<2	24.0	2.6	20.3	<2	4.0	<2	<2	59.1
Site 6	6.7	<2	24.6	2.8	23.1	<2	4.3	<2	<2	61.4
Site 7	6.6	<2	22.2	2.5	21.4	<2	4.3	<2	<2	57.1
Site 8	2.1	<2	21.4	2.5	21.7	<2	5.0	<2	<2	52.8
Site 9	4.2	<2	21.5	2.5	22.0	<2	4.4	<2	<2	54.6
Site 10	8.6	<2	21.1	2.5	21.3	<2	4.5	<2	<2	57.9
Site 11	7.1	<2	23.0	2.6	21.3	<2	4.5	<2	<2	58.6
Site 12	9.8	<2	24.9	2.5	22.1	<2	4.1	<2	<2	63.5
Site 13	8.4	<2	21.6	2.5	21.5	<2	4.0	<2	<2	58.0
Site 14	6.6	<2	23.1	2.6	21.8	<2	4.4	<2	<2	58.4

Table A.15

Haloacetic acid concentrations (µg/L) for 3/11/03, while using free chlorine.

Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
Site 1	11.8	<2	21.3	2.5	21.8	<2	4.3	<2	<2	61.5
Site 2	8.6	<2	25.6	2.2	30.9	<2	5.1	<2	<2	72.4
Site 3	4.0	<2	38.7	3.2	44.4	<2	6.0	<2	<2	96.2
Site 4	10.3	<2	36.0	2.8	48.7	<2	6.4	<2	<2	104
Site 5	5.8	<2	34.4	3.1	40.0	<2	7.1	<2	<2	90.5
Site 6	7.0	<2	33.5	3.3	38.3	<2	6.5	<2	<2	88.6
Site 7	10.0	<2	28.1	2.7	34.6	<2	5.7	<2	<2	81.1
Site 8	11.4	<2	26.2	3.1	31.5	<2	6.1	<2	<2	78.3
Site 9	10.3	<2	27.1	3.2	32.6	<2	6.5	<2	<2	79.6
Site 10	9.2	<2	25.4	3.0	28.5	<2	5.6	<2	<2	71.8
Site 11	6.1	<2	34.7	3.4	40.5	<2	6.4	<2	<2	91.1
Site 12	3.6	<2	36.6	3.5	38.7	<2	5.6	<2	<2	88.0
Site 13	10.1	<2	27.7	3.4	32.8	<2	6.0	<2	<2	80.0
Site 14	6.6	<2	34.9	3.4	40.6	<2	6.6	<2	<2	92.1

Table A.16

Haloacetic acid concentrations (µg/L) for 4/29/03, while using combined chlorine.

Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
Site 1	3.0	<2	26.7	<2	28.7	<2	4.2	2.4	<2	64.9
Site 2	2.6	<2	28.4	<2	26.9	<2	3.4	<2	<2	61.3
Site 3	4.5	<2	39.9	<2	32.0	<2	3.5	2.4	<2	82.3
Site 4	4.2	<2	33.9	<2	31.2	<2	3.4	2.3	<2	74.8
Site 5	4.0	<2	33.2	<2	30.5	<2	3.7	2.4	<2	73.8
Site 6	3.9	<2	29.8	<2	29.9	<2	3.6	2.2	<2	69.5
Site 7	2.9	<2	28.4	<2	28.1	<2	3.8	2.2	<2	65.4
Site 8	3.5	<2	29.2	<2	31.2	<2	4.4	2.4	<2	70.6
Site 9	3.0	<2	27.7	<2	30.7	<2	4.2	2.3	<2	67.9
Site 10	4.6	<2	27.3	<2	29.6	<2	4.2	2.4	<2	68.0
Site 11	4.3	<2	32.4	<2	31.1	<2	3.9	2.2	<2	73.9
Site 12	5.3	<2	34.2	<2	32.4	<2	3.8	<2	<2	75.7
Site 13	4.7	<2	30.0	<2	30.8	<2	4.1	<2	<2	69.6
Site 14	4.9	<2	31.3	<2	31.9	<2	3.9	<2	<2	72.0

Appendix B

Additional Results

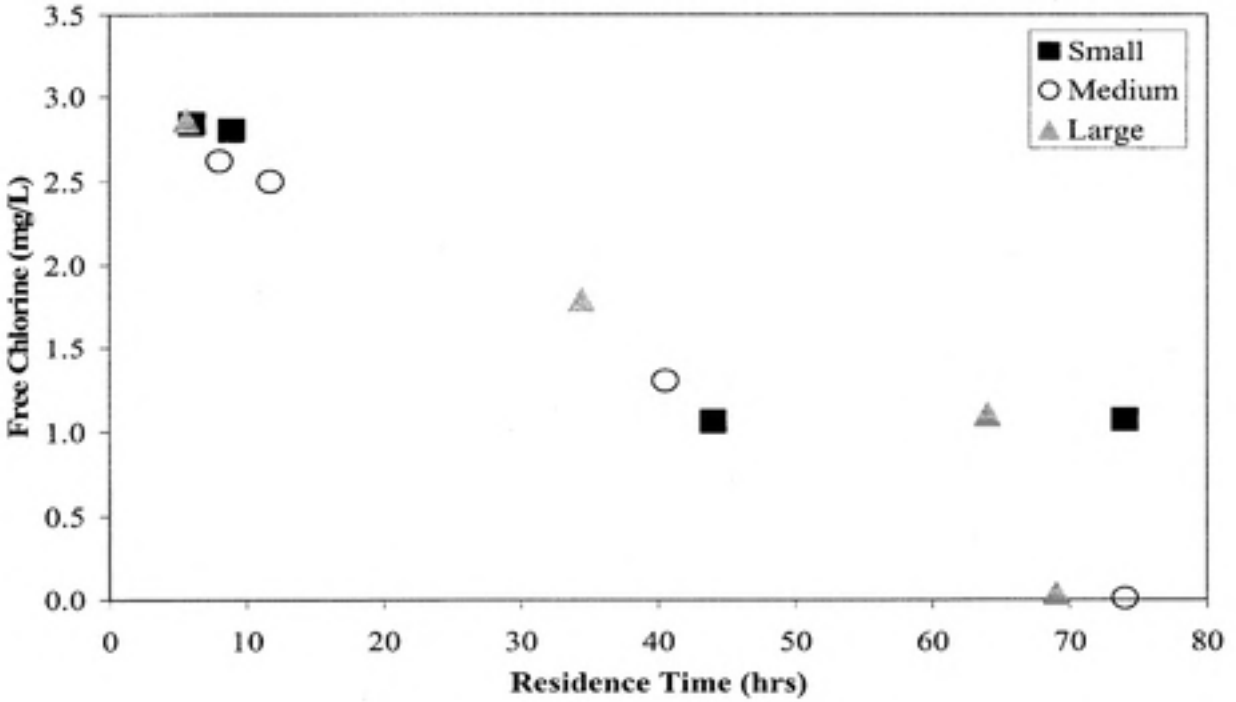

Figure B.1 Free chlorine concentrations in small, medium, and large diameter pipe over the range of residence times on 3/11/03.

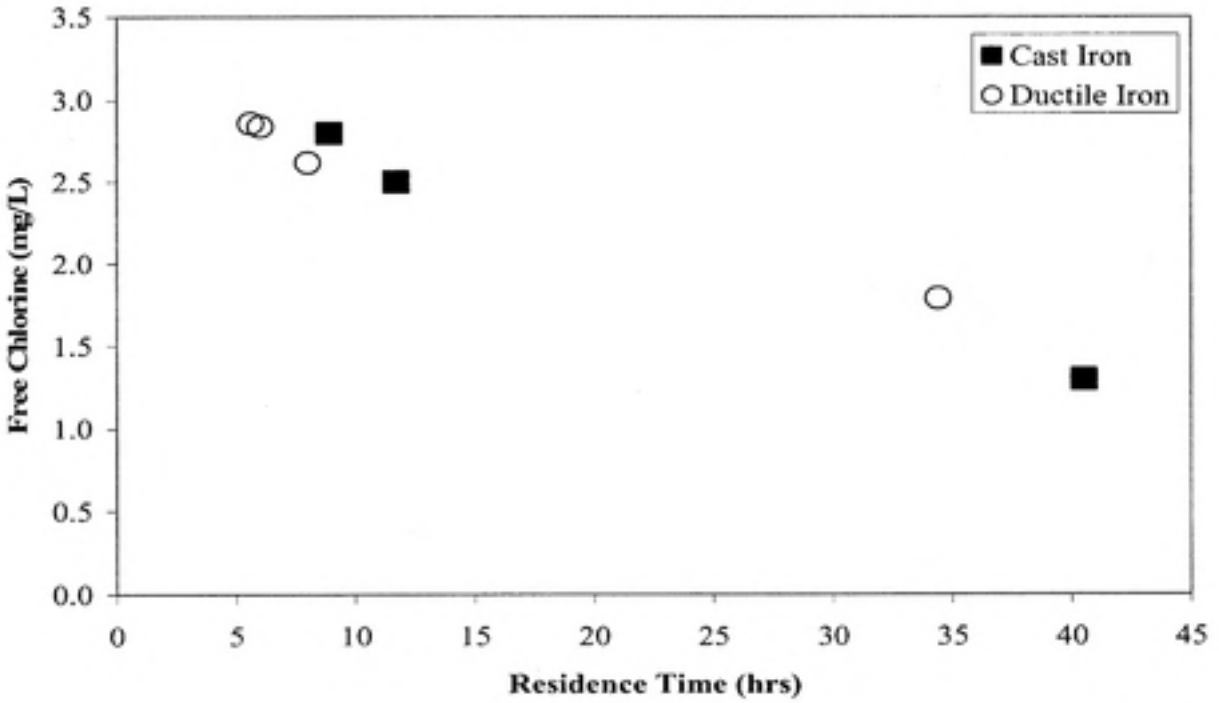

Figure B.2 Free chlorine concentrations in cast iron and ductile iron pipe for low and medium residence times on 3/11/03.

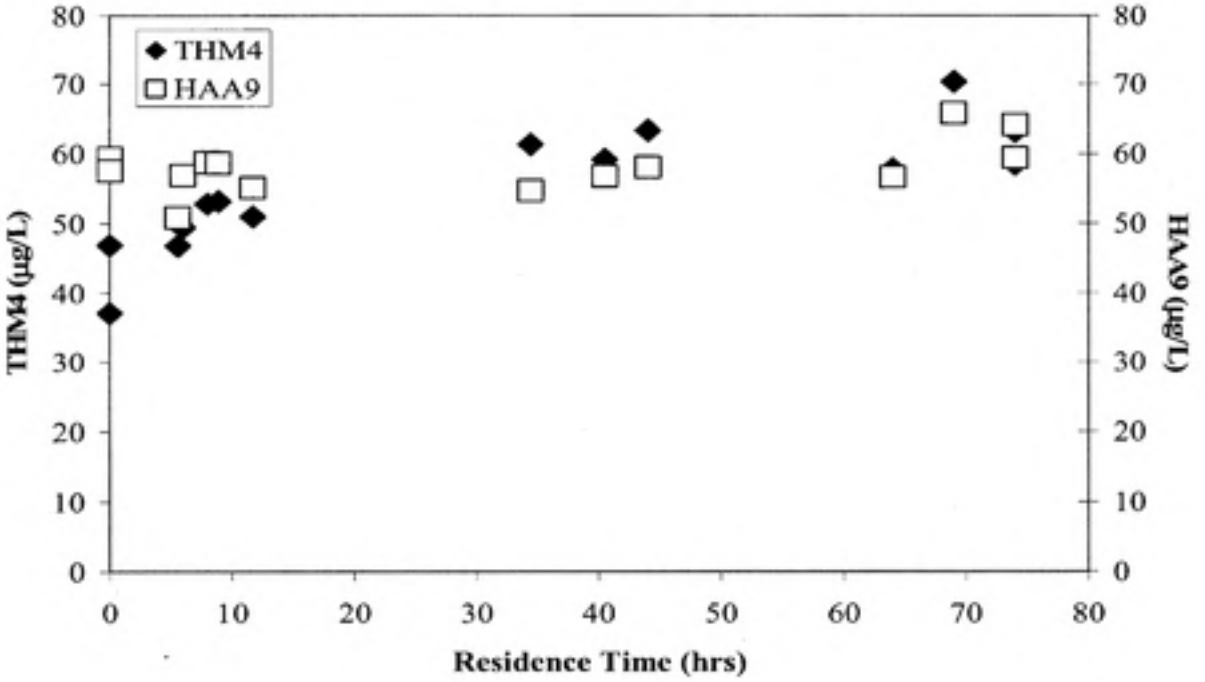

Figure B.3 Comparison of the HAA9 and THM4 concentrations on 2/11/03 while using combined chlorine for secondary disinfection.

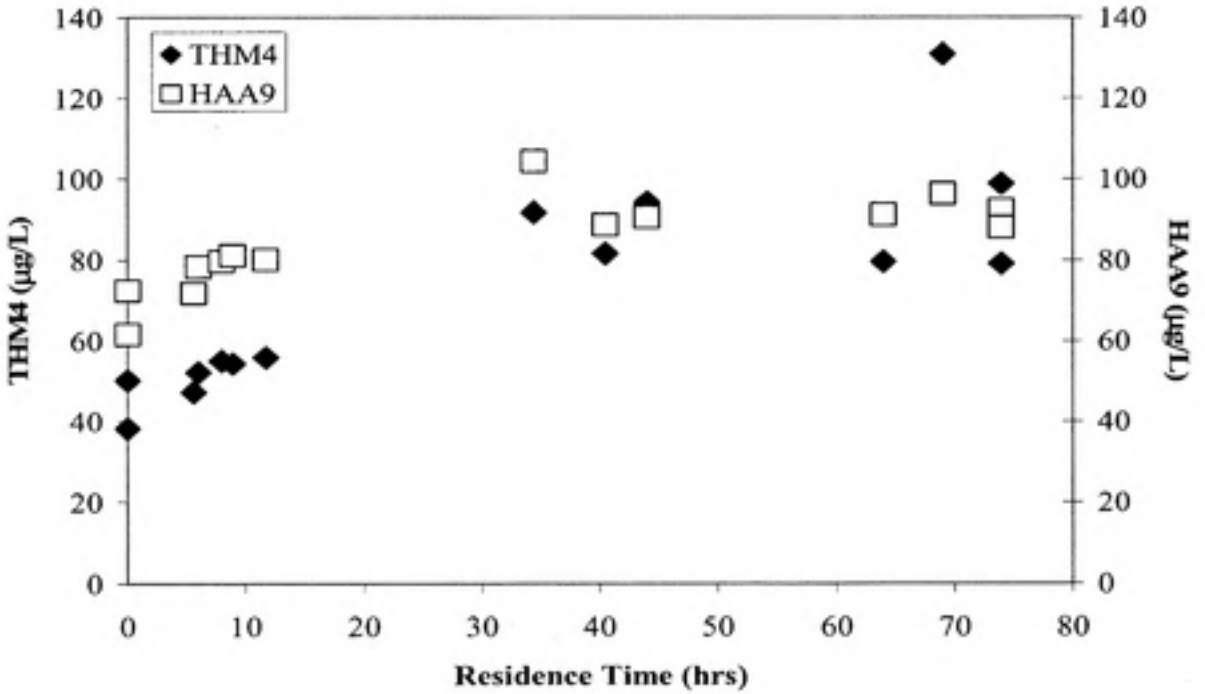

Figure B.4 Comparison of the HAA9 and THM4 concentrations on 3/11/03 while using free chlorine for secondary disinfection.

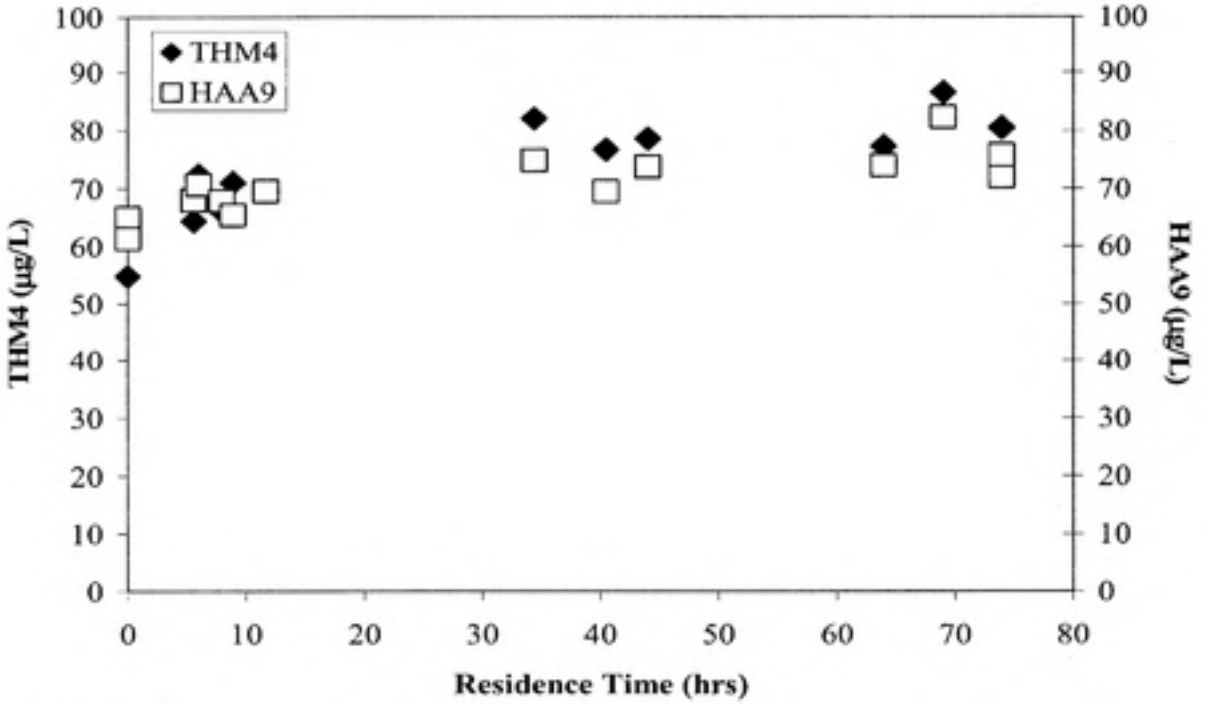

Figure B.5 Comparison of the HAA9 and THM4 concentrations on 4/29/03 while using combined chlorine for secondary disinfection.

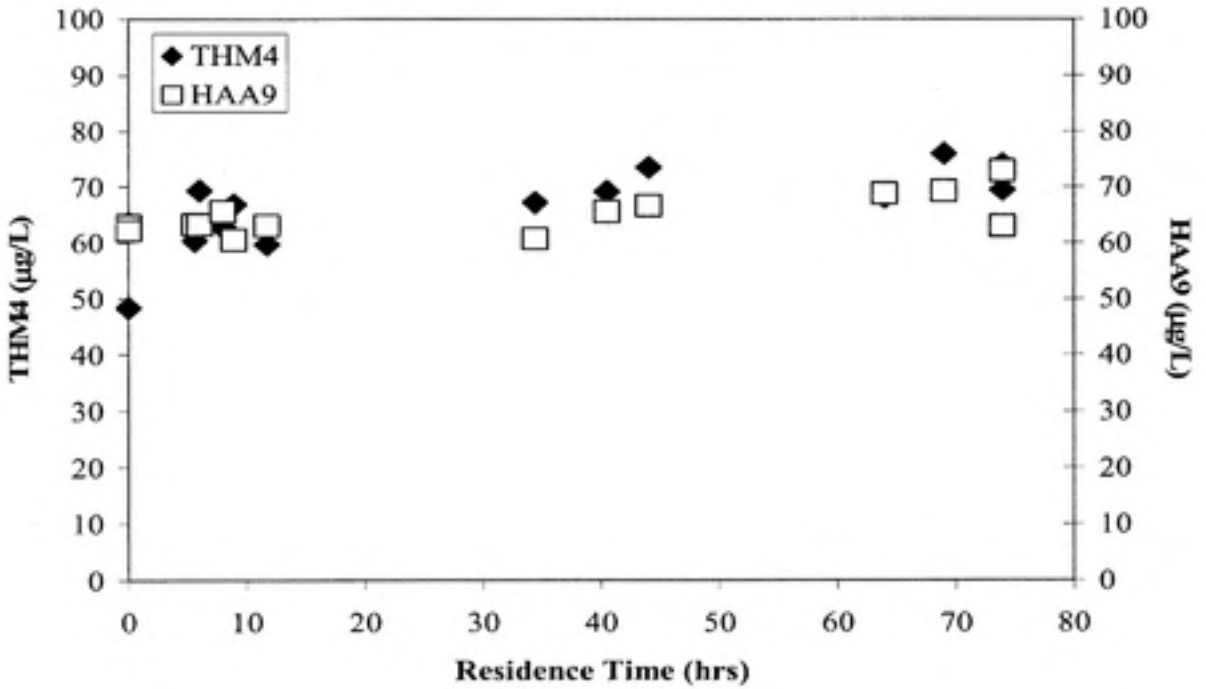

Figure B.6 Comparison of the HAA9 and THM4 concentrations on 5/20/03 while using combined chlorine for secondary disinfection.

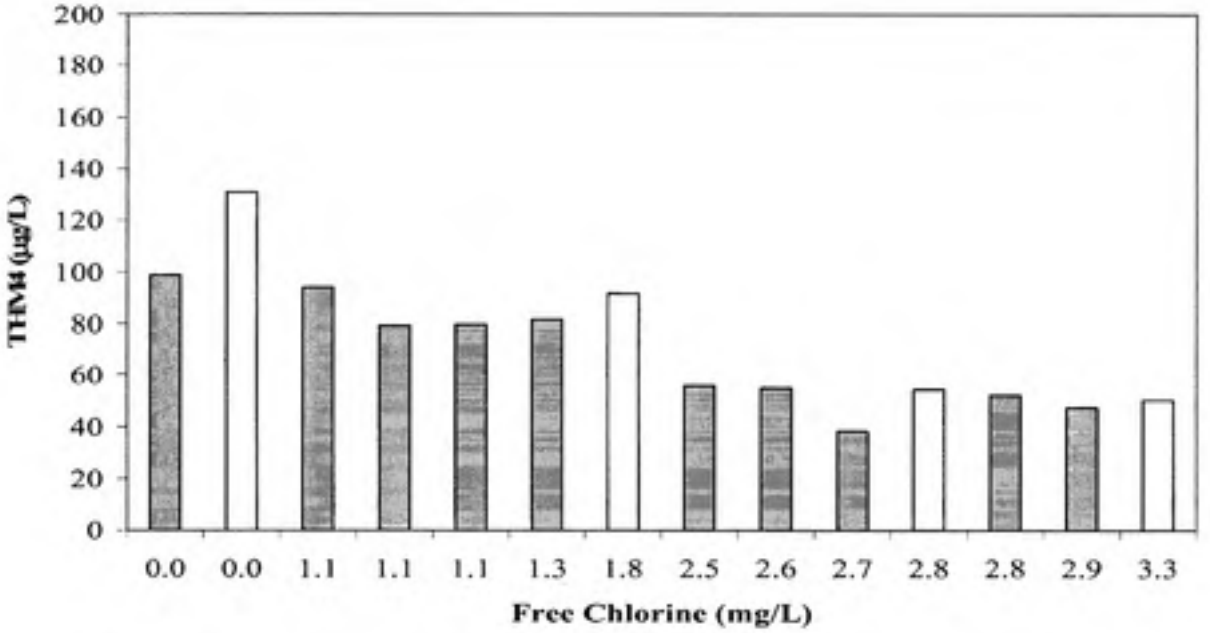

Figure B.7 THM4 concentrations and corresponding free chlorine concentrations on 3/11/03 while using free chlorine for secondary disinfection. Sample sites receiving Site 1 point of entry water are in gray, and locations receiving Site 2 point of entry water are in white.

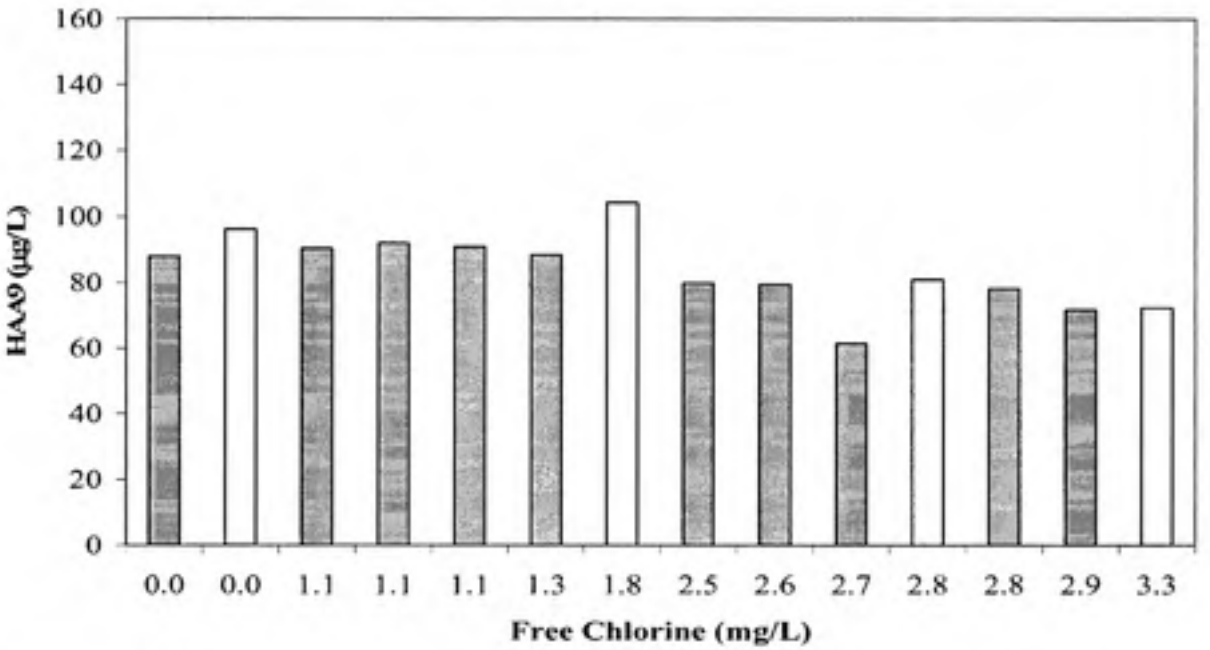

Figure B.8 HAA9 concentrations for corresponding free chlorine concentrations on 3/11/03 while using chlorine for secondary disinfection. Sample sites receiving Site 1 point of entry water are in gray, and locations receiving Site 2 point of entry water are in white.

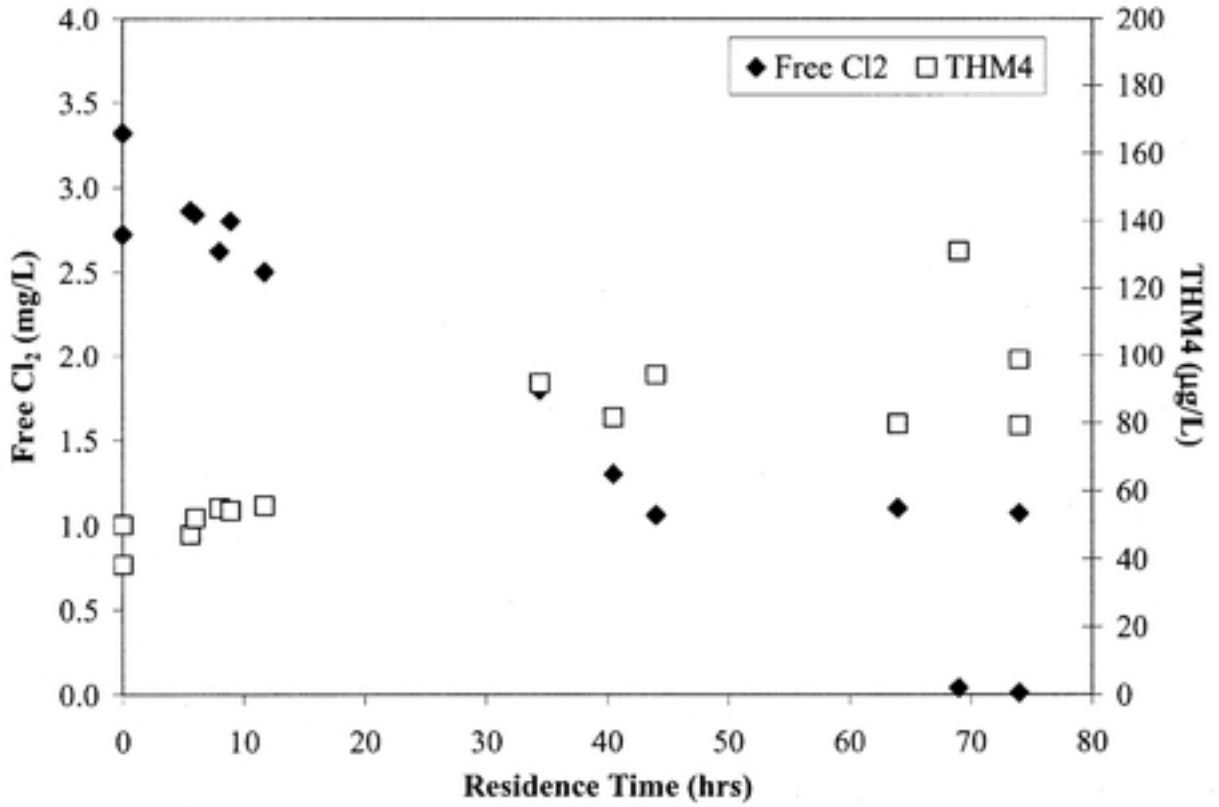

Figure B.9 Comparison between THM4 and free chlorine concentrations for all residence times on 3/11/03 while using free chlorine for secondary disinfection.

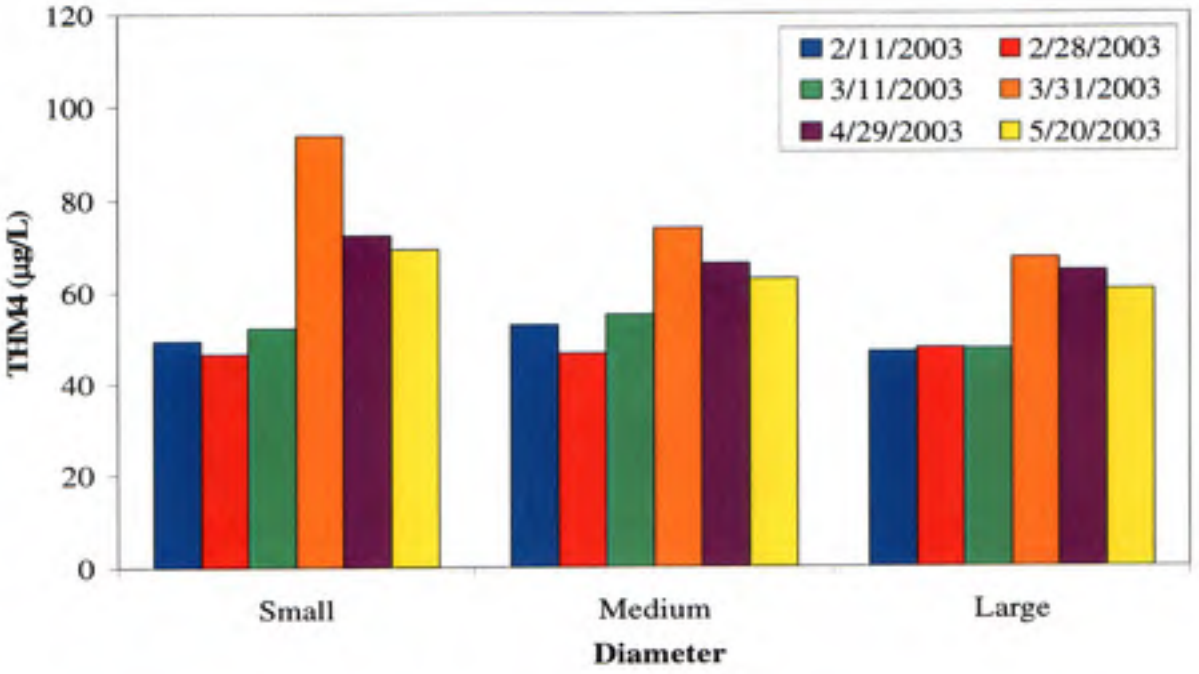

Figure B.10 Variation in THM4 concentrations with varying pipe diameters for low residence time, ductile iron pipes receiving Site 1 point of entry water.

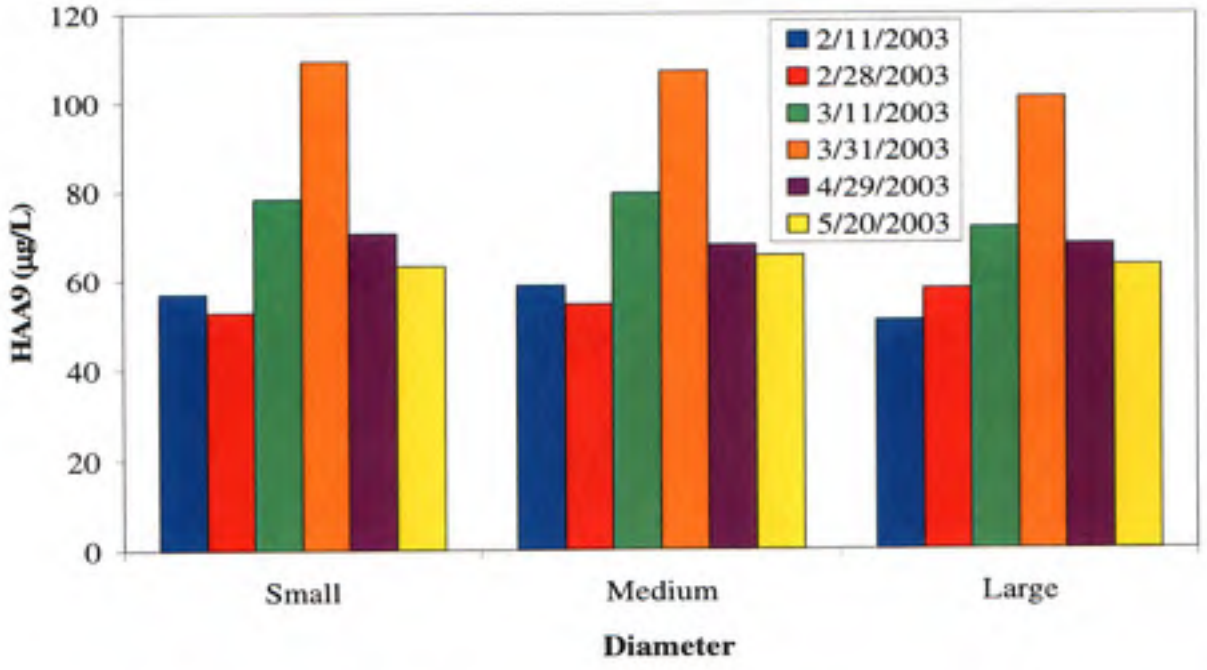

Figure B.11 Variation in HAA9 concentrations with varying pipe diameters for low residence time, ductile iron pipes receiving Site 1 point of entry water.

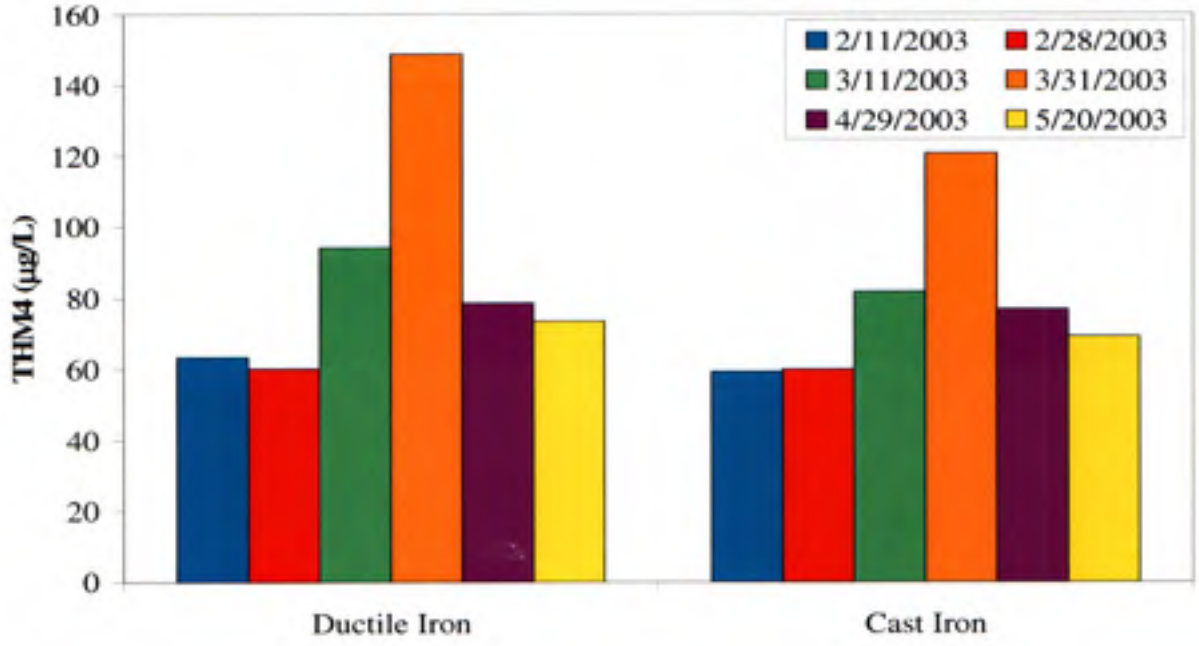

Figure B.12 Comparison of THM4 concentrations in ductile iron and cast iron for medium residence time, medium diameter pipes with Site 1 point of entry water.

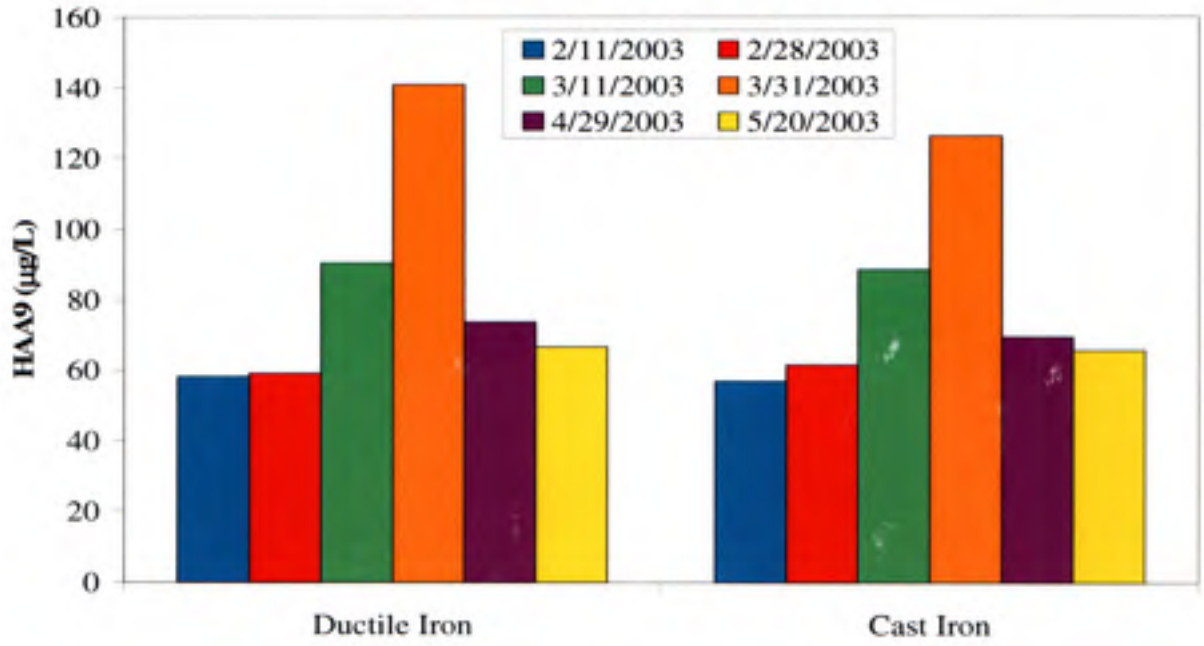

Figure B.13 Comparison of HAA9 concentrations in ductile iron and cast iron for medium residence time, medium diameter pipes with Site 1 point of entry water.

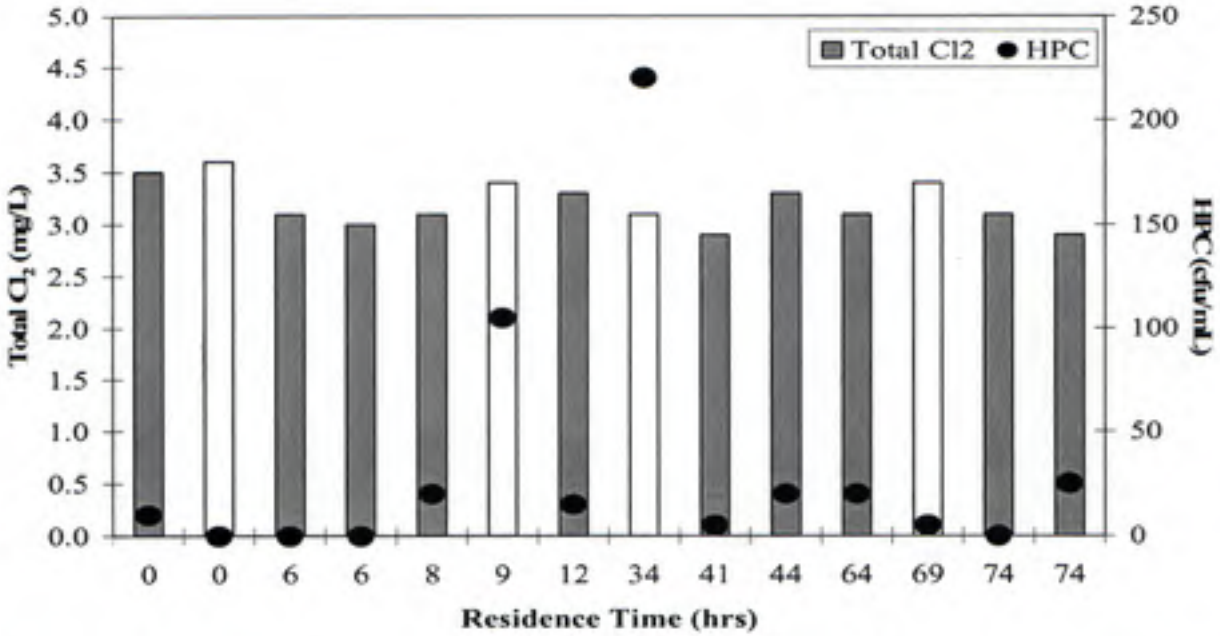

Figure B.14 Comparison of the total chlorine concentrations and HPCs for all residence times during chloramination on 2/11/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

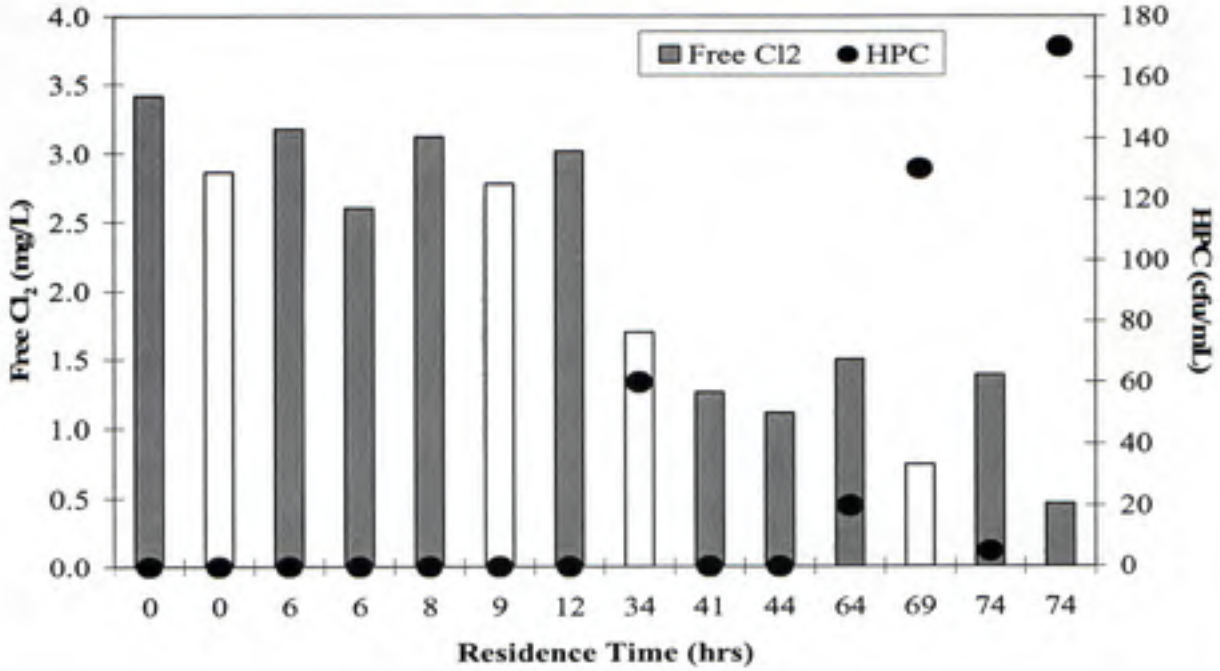

Figure B.15 Comparison of the free chlorine concentrations and HPCs for all residence times during chlorination on 3/31/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

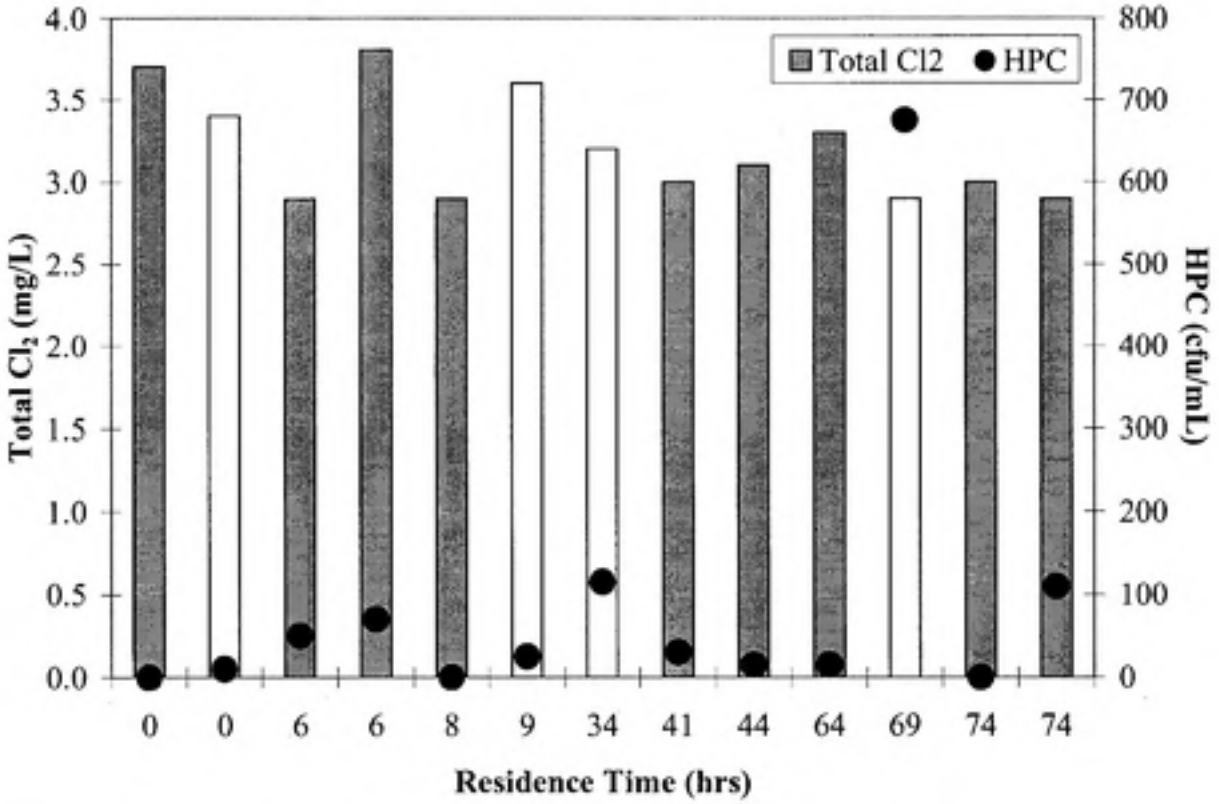

Figure B.16 Comparison of the total chlorine concentrations and HPCs for all residence times during chloramination on 4/29/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

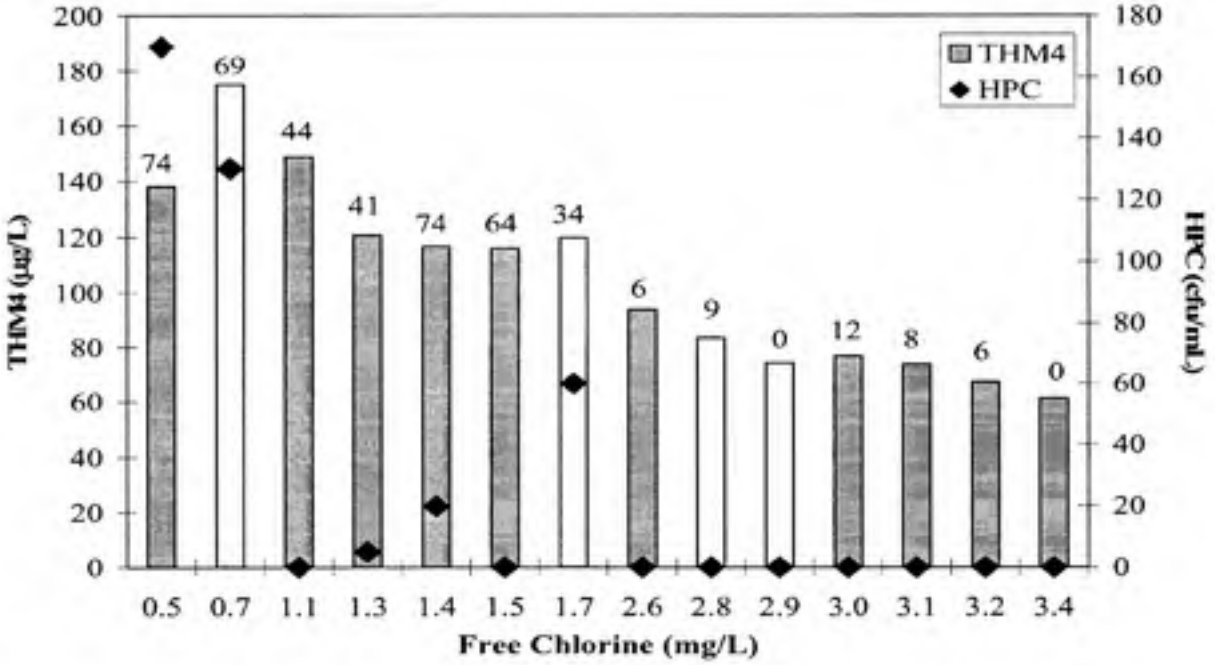

Figure B.17 Comparison among THM4, HPC, and free chlorine concentrations during chlorination on 3/31/03. Residence times are listed above each bar. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

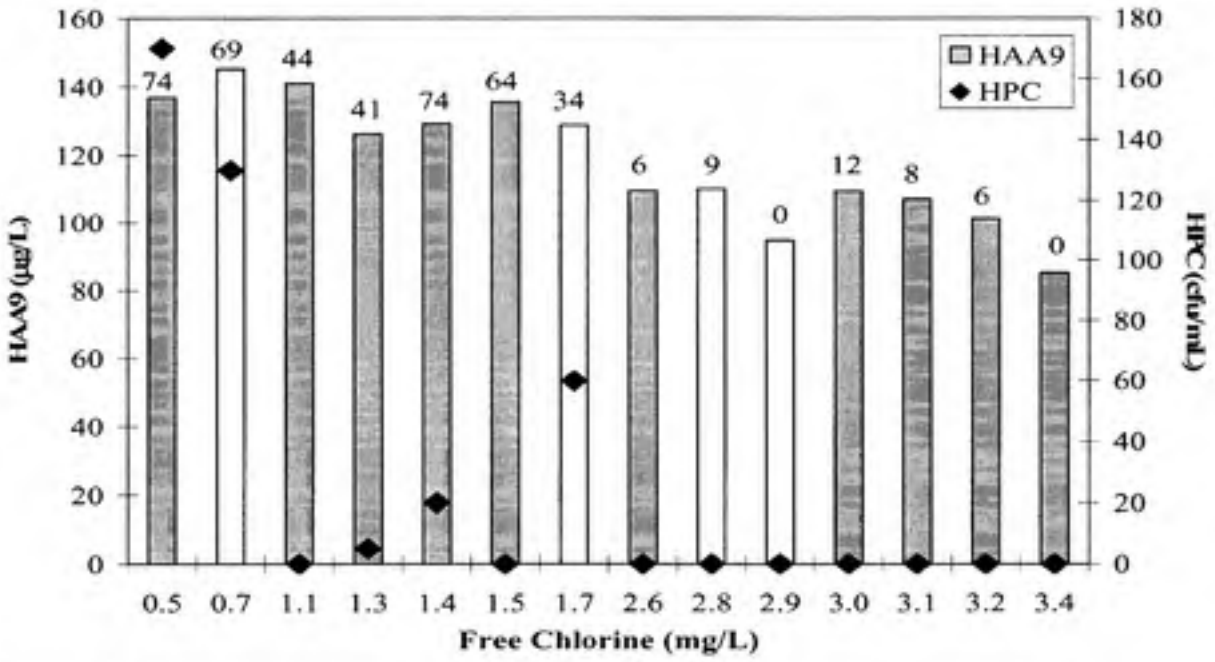

Figure B.18 Comparison among HAA9, HPC, and free chlorine concentrations during chlorination on 3/31/03. Residence times are listed above each bar. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

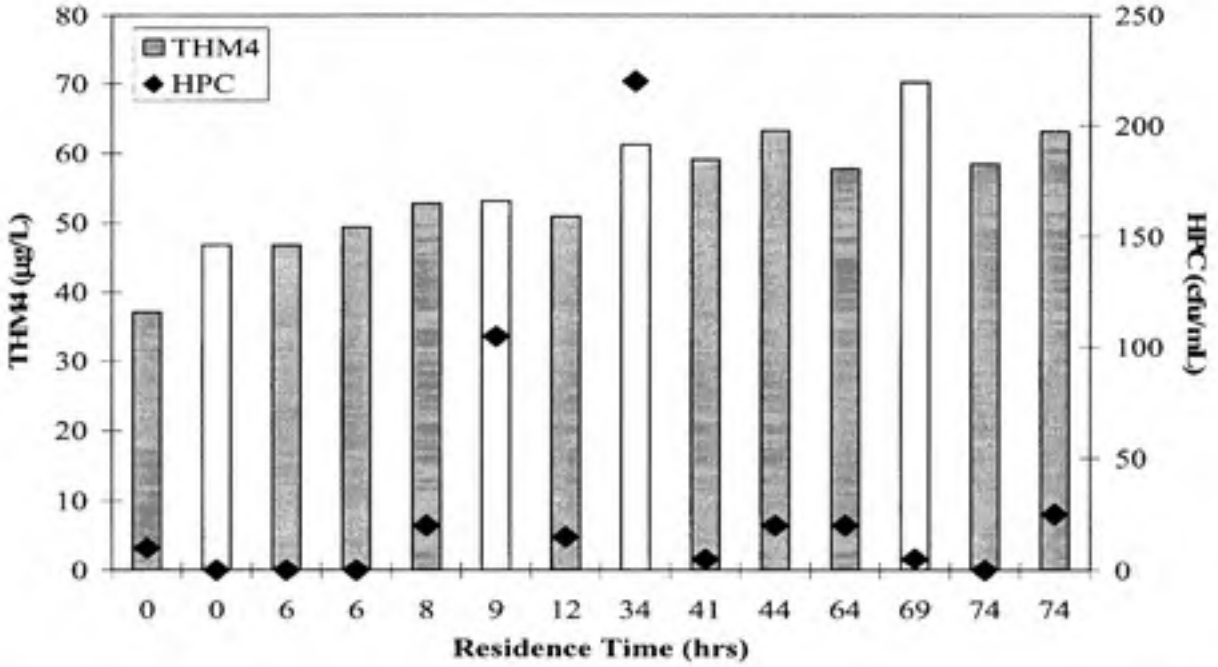

Figure B.19 Comparison between THM4 concentrations and HPCs for all residence times during chloramination on 2/11/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

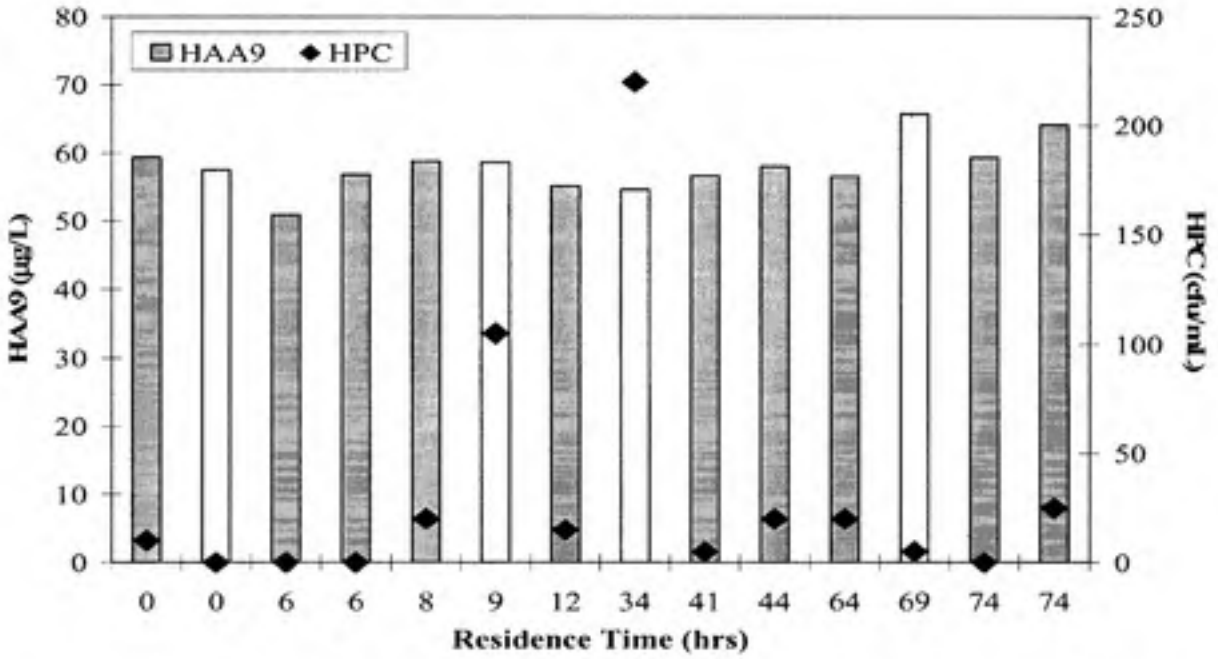

Figure B.20 Comparison between HAA9 concentrations and HPCs for all residence times during chloramination on 2/11/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

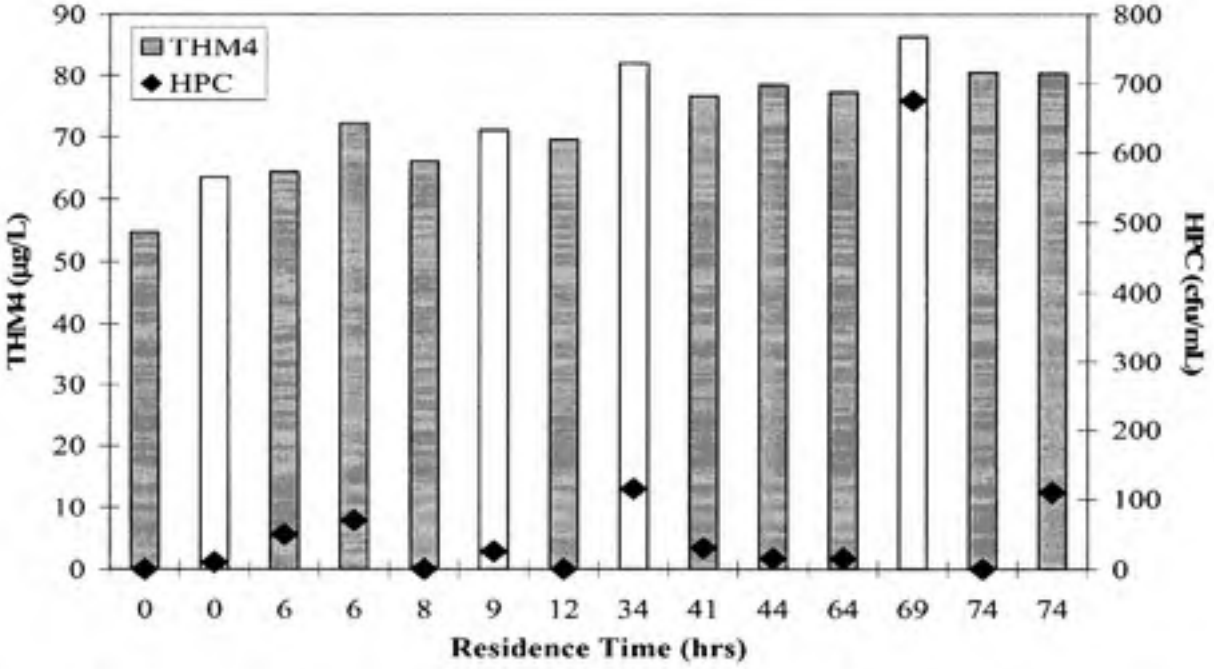

Figure B.21 Comparison between THM4 concentrations and HPCs for all residence times during chloramination on 4/29/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

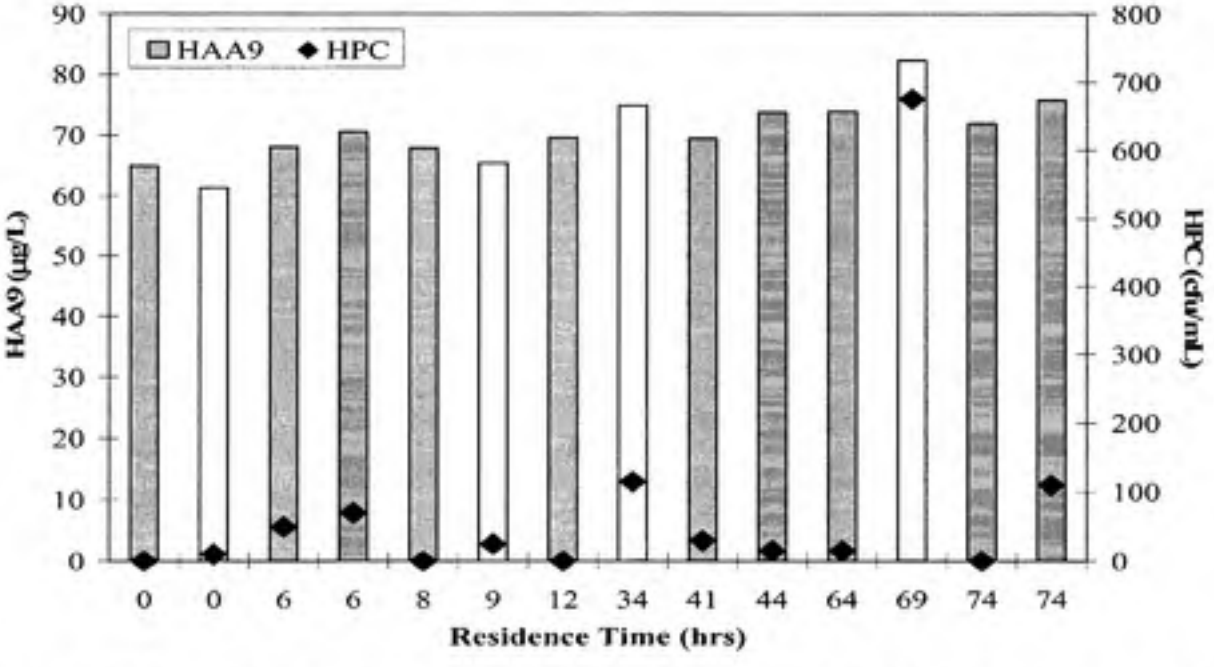

Figure B.22 Comparison between HAA9 concentrations and HPCs for all residence times during chloramination on 4/29/03. Site 1 point of entry water is indicated by gray bars, while Site 2 point of entry water is indicated by white bars.

Appendix C

Batch Kinetic Test Results

Table C.1

Batch kinetic data for sampling conducted on 3/11/03 at a temperature of 7.4°C.

Residence Time (hrs)	Total Cl_2 (mg/L)	Free Cl_2 (mg/L)	THM4 (µg/L)	HAA9 (µg/L)
Point of Entry	3	2.72	38.3	61.5
24	2.8	2.38	56.0	83.2
48	2.7	2.28	57.8	84.9
72	2.7	2.22	54.6	92.8

Table C.2

Batch kinetic data for sampling conducted on 4/29/03 at a temperature of 14.5°C.

Residence Time (hrs)	Total Cl_2 (mg/L)	THM4 (µg/L)	HAA9 (µg/L)
Point of Entry	3.7	54.8	64.9
24	3.4	71.6	72.1
48	3.6	69.8	52.2
72	3.2	65.4	66.0

Table C.3

Batch kinetic data for sampling conducted on 5/20/03 at a temperature of 16°C.

Residence Time (hrs)	Total Cl_2 (mg/L)	THM4 (µg/L)	HAA9 (µg/L)
Point of Entry	2.9	48.3	63
24	2.1	57.4	60.1
48	2.3	53.9	60.5
72	1.8	49.3	60.4